

TECHNOLOGY UTILIZATION

JOINING CERAMICS AND GRAPHITE TO OTHER MATERIALS

A REPORT



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JOINING CERAMICS AND GRAPHITE TO OTHER MATERIALS

A REPORT

By H. E. Pattee,
R. M. Evans, and R. E. Monroe

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Foreword

The present report is one of a series by which the NASA Office of Technology Utilization is sharing aerospace technical information with individuals, Government agencies, and private concerns engaged in other endeavors. In reviewing advances resulting from both Government and private studies of the technology of joining ceramics and graphite to metals and other materials, the report emphasizes ceramic-to-metal joining as practiced in the electronic industry where most of the developments originated. The same procedures, however, can be followed to meet the needs of many other industries.

The technology of joining graphite to other materials has been developed principally in response to requirements of the aerospace and nuclear industries. Much of the knowhow used in joining ceramics is also applicable to the joining of graphite.

In reviewing materials selection, joint configuration, surface preparation, and other facets of joining problems, the authors discuss both bonding theories and methods of evaluating joints.

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CHAPTER 1

Introduction

Ceramic-to-metal seals and joints are assuming increasing importance in today's technology, and it is safe to predict that their uses will increase in the future as the advantages of ceramics as construction materials are realized. For example, when the first space station is established in outer space, ceramic-to-metal joints will play a significant role in its construction and operation. Nuclear- and solar-power devices will probably be used to provide energy, and ceramic-to-metal joints will be needed in the equipment that converts nuclear and solar energy to electrical power. Similarly, ceramic coating may be used to provide the emissivity required to control and maintain the proper temperature level within the space station structure. The performance of the space vehicles now depends on the ability of ceramic-to-metal joints to provide strength, erosion resistance, and high-temperature protection where needed.

BACKGROUND

Since its beginnings in the late 1930's, the technology of joining ceramics to metals and other materials has progressed steadily. Like other materials-joining processes, the joining of ceramics to other materials was initially more an art than a science; the proprietary nature of developments in this field aggravated the situation. During and after World War II, however, efforts to develop procedures that could be used to produce reliable joints between ceramics and metals became serious. Much has been accomplished during the intervening years toward establishing a joining technology based on sound fundamental principles and an understanding

of the reactions that occur during joining. However, the basic nature of the bond-producing mechanism still eludes investigators, although they have advanced many theories to explain it.

Ceramic-to-metal joining, as we know the process today, had its industrial origins during World War II in Germany, where, under wartime conditions, it was recognized that vacuum tubes with improved performance and reliability could be produced by substituting ceramics for glass. Pulfrich (Telefunken) and Vatter (Siemens and Halske, A. G.) established procedures to metallize ceramics, thus producing surfaces that, in subsequent joining operations, could be wet by brazing alloys. Numerous domestic and foreign patents on metallizing and joining techniques were issued to Pulfrich, Vatter, or the firms that employed them in the middle and late 1930's; some of the most significant of these patents are listed in references 1 to 9.* While the results obtained by Pulfrich and Vatter are somewhat crude in the light of current developments, their basic concepts are still valid, and their metallizing procedures, or modifications thereof, are used extensively to prepare ceramic surfaces for joining. The advantages associated with the use of ceramics for the envelopes, internal structural supports, and output windows of vacuum tubes are as follows:

1. Ceramic tubes can be outgassed at higher temperatures than glass tubes. For ceramic tubes, the permissible outgassing temperature depends on the melting temperature of the filler metal used in the ceramic-to-metal seal and the degree to which the thermal expansion coefficient

* References appear at the end of this report.

cients of the joint members are matched. Because of the increased vapor pressure of the residual impurities, outgassing at high temperatures is more effective and promotes longer tube life and increased emission.

2. Because of the high-temperature seal, ceramic tubes withstand higher temperatures than glass tubes of similar dimensions.

3. Ceramic tubes are mechanically stronger and less sensitive to thermal shock than glass tubes. Thus, performance is less affected by rigorous service conditions.

4. Ceramic components can be ground to the precise tolerances required for vacuum-tube construction.

5. Ceramic materials have very low electrical losses at high frequencies. They are well suited for use as output windows in microwave tubes, because they can pass maximum amounts of power while separating evacuated and unevacuated areas of the tubes.

However, the use of ceramics in vacuum-tube construction is not without disadvantages, some of which are cited below:

1. The joint configurations for ceramic-to-metal seals are somewhat limited because ceramics have high compressive, but low tensile strengths. Compression seals are used wherever possible; butt-seals are satisfactory if tensile stresses are minimized.

2. Careful selection of the seal's ceramic and metal members is necessary to obtain a good match of the thermal expansion coefficients and the expected temperature range.

3. Most ceramics are opaque, so that the alignment of electrode assemblies cannot be inspected after assembly or operation; however, some high-purity alumina ceramics are nearly transparent.

4. Flaws initially present or produced during machining are difficult to detect.

5. Metallizing and joining operations are costly, because multi-step procedures must take place at high temperatures in controlled-atmosphere or vacuum furnaces.

Nevertheless, the advantages of ceramics for vacuum-tube applications far outweigh the problems. Most problems can be eliminated or minimized by proper materials selection and

careful joint design; in many instances, ceramics are the only materials that fit a particular application.

Ceramic-to-metal joints were first used extensively in the construction of vacuum tubes for critical applications. The electronics industry is still the largest user of such seals, but other industries use ceramics increasingly as structural components, coatings, and strengthening agents in metals. When used as structural components, ceramic-to-metal joints may be required to complete an assembly or provide sealing. Some applications that indicate the versatility of ceramics in other than the vacuum-tube industry are outlined in the following paragraphs.

Because of their inertness in many corrosive environments, ceramics are used as seals in fuel cells and other devices that convert chemical, nuclear, or thermionic energy to electricity. In a current program to develop a nuclear power source to produce electrical energy for space applications, a large thin-walled ceramic cylinder is being used in the fabrication of a "bore" seal. The ceramic-to-metal seal is required to isolate the electrical sections (windings, armature, and poles) of a turbine-driven generator designed to operate in corrosive liquid-metal vapors (ref. 10). Bristow, Grossman, and Kaznoff have also developed special ceramic-to-metal seals for a cesium vapor-filled thermionic converter (ref. 11).

In addition to high-temperature strength and resistance to corrosive media, certain ceramics possess properties that make them attractive for use in high-temperature nuclear reactors of advanced design. Since some of the metals used for metallizing are unsuitable for reactor environments, Fox and Slaughter investigated the characteristics of several experimental filler metals to be used in joining the oxides of aluminum, beryllium, and uranium to themselves and to metals without previous metallizing (ref. 12). Simulated fuel-element assemblies were fabricated from alumina (Al_2O_3) and beryllia (BeO) using a Ti-49Cu-2Be brazing filler metal.

Extensive investigations of ceramics as struc-

tural components in gas turbines and rocket engines were conducted during the 1950's. In attempting to use oxide ceramics and cermets for turbine blades and buckets, the direct substitution of ceramics for metals was largely unsuccessful, because ceramics have poor impact and tensile properties. For such applications, ceramics have proved most useful in providing oxidation and wear-resistant metal coatings.

Extensive research has been conducted on the use of ceramics for the dispersion-hardening of metals; thoriaed nickel (TD) and sintered aluminum powder (SAP) are the best known alloys of this type. For example, SAP is an aluminum material that maintains its strength at higher temperatures than other aluminum alloys. It contains a dispersed phase of up to 15-weight percent aluminum oxide. SAP can be extruded, rolled, forged, and drawn by conventional metalworking techniques. While care in surface preparation must be observed, SAP can be soldered, brazed, and welded to itself and other metals. SAP has been used in various forms by the automotive, aircraft, and nuclear industries. Currently, there is great interest in strengthening metals with single-crystal alumina fibers or whiskers (ref. 13).

Because of their transparency to microwaves, ceramics are used extensively for radomes to enclose radar antenna equipment on supersonic aircraft. Plastic radomes were suitable until sonic speeds were achieved when air friction and impact from dust and raindrops in the atmosphere created problems. Materials for radome fabrication are generally limited to high-alumina and some refractory glasses. Small radomes can be cast or formed; large radomes are more difficult to produce because of close tolerances on shape, wall thickness, and dielectric constant. In a recently completed program, engineers at the Whittaker Corporation used mosaic techniques to fabricate a large radome over a removable form; the radome was 37 inches in diameter and 8 feet high (ref. 14). Precisely cut 97.6-percent alumina tiles were assembled around the form and cemented in place. After assembly, the form was removed and the radome was placed in a firing

tool. Differential tooling was used to apply pressure during firing.

Ceramics are also used as friction materials for brakes, clutches, and other energy-absorbing devices (ref. 15); coatings for nuclear fuel particles (refs. 16 and 17); constituents in high-temperature adhesives (refs. 18 to 20); and ablation materials and coatings for metals.

While some degree of joining is required in ceramic-to-metal seals, ceramic-coated metals, ceramic-filled metal structures, ceramic-fiber reinforced metals, cermets, and composites, the mechanism of joining varies from chemical and/or electronic bonding to mechanical interlocking of ceramic particles with a metal substrate.

PURPOSE AND SCOPE

In discussing the joining of bulk ceramics to metals and other materials, this report will emphasize ceramic-to-metal joining as applied in the electronics industry, because more research has been initiated by this industry than any other; as a result, extensive information is available. However, the techniques developed for joining ceramics to the metals of interest to the electronics industry can usually be applied to other materials as well.

The report will summarize data on joining ceramics to other materials available from Government and industrial research. Much of the research was prompted by a need to develop joining or sealing techniques for specific applications which will be related throughout the report in hope that the information can be applied to applications that are similar or involve unusual materials or service conditions.

In addition to an extensive review of the important considerations of ceramic-to-metal joining, the technology of joining graphite to other materials will be discussed in some detail. Ceramics and graphite have much in common. Both materials have excellent high-temperature properties and are chemically inert in many corrosive media; as a result, ceramics and graphite have been considered for missile components where materials that maintain their strength at high temperatures in a corrosive or erosive environment are required. Brazing filler metals do

not wet either material readily, so special joining techniques are required.

The sources of information for this report included reports of Government and industry filed by the Defense Ceramics Information Center (DCIC) and the Defense Metals Information Center (DMIC), technical literature on joining ceramics and graphite, various engineering indexes, libraries of the Columbus Laboratories of Battelle Memorial Institute, and personal files. The literature searches included a Defense Documentation Center (DDC) search, a Redstone Scientific Information Center (RSIC) search, a NASA Scientific and Technical Information Facility search, and a DD-1498 Data Bank search. These searches were reviewed and about 100 reports on Government-sponsored re-

search activities were requested and studied. Selected industrial contacts were also made to acquire information on other current investigations.

Vatter (ref. 25) and Jenkins (ref. 26) have published excellent reviews of the historical development of ceramic-to-metal seals. In 1953, a symposium on ceramics and ceramic-to-metal seals was held; the papers presented there appeared in various issues of *Ceramic Age* in 1954 and offer a good picture of the technology of that date. More recent reviews were published by Van Houten (ref. 27) in 1959 and by Clark, Ritz, and Girard (ref. 28) in 1965. Kohl has discussed developments in ceramic-to-metal joining on several occasions; his latest publication was dated in 1967 (ref. 29).

CHAPTER 2

Materials for Ceramic-to-Metal Joints

CERAMICS

It is easier to discuss the characteristics and properties of ceramics than to define them. Kohl states that ceramics is a "term used to describe a variety of solids of different compositions that have attained a crystalline state by the firing of inorganic nonmetallic materials" (ref. 29). The raw materials that form ceramics have a crystalline structure before firing and retain this property after firing. Glasses are not ceramics according to this definition, because a noncrystalline solid is formed after the glass constituents are fired. By recently developed processes some glasses can be converted to ceramics when certain nucleating agents are added to the glass constituents.

The technology of formulating ceramics has developed tremendously in the last decade in response to the requirements of industry. The selection of ceramics was once limited mainly to multiphase silicate ceramics; now, one may select carefully from a wide variety of oxides, borides, nitrides, carbides, and silicides on the basis of specific service requirements.

The raw materials from which ceramics are made have changed significantly in recent years. The first ceramics used in vacuum tubes were the steatites, multiphase silicate ceramics of the type $\text{MgO} \cdot \text{SiO}_2$; the quality of these ceramics varied according to the raw materials. Because the reactions during the firing process were not well understood, the proportions of the ceramic constituents were not exact, and precise control of the production process was lacking. Pulfrich noted that metallizing and brazing tests with representative samples from a production run of ceramics were necessary to ensure sound

ceramic-to-metal seals; mechanical and electrical tests were conducted also as a quality control measure (ref. 20).

Many of the problems associated with the quality of early ceramics were related to the proprietary nature of developments in this field. The sources of raw materials were kept secret, and the ceramic compositions and processing details were not openly discussed. The Government-sponsored research undertaken after World War II to investigate and improve the techniques of ceramic-to-metals sealing did much to dispel this secrecy. More recent research has been concentrated on the effects of impurities and firing cycle on the basic properties of ceramics; the steady improvement in ceramic quality has demonstrated the value of disseminating the results of research.

A number of relatively inexpensive multiphase silicate ceramics were developed over the years. In addition to the low-loss steatites, these included forsterite ($2\text{MgO} \cdot \text{SiO}_2$), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), and zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$). About 35 years ago, the single-phase oxide ceramics were developed, the most important of which are alumina (Al_2O_3) and beryllia (BeO). High-alumina materials were originally used as sparkplug bodies because of their resistance to thermal shock. After World War II, the superior properties of alumina for vacuum-tube applications were recognized, and studies were begun to develop techniques for using alumina effectively. Unlike the multiphase silicate ceramics that are formed from plastic clays, the metal-oxide ceramics are produced in useful shapes by sintering a loose mass of oxide grains. During sintering, molecular forces acting be-

tween adjacent particles result in the formation of a bonded-crystal network. Strong bonds between the initially loose grains occur without gross melting or additional binders.

Alumina is attractive for vacuum-tube applications because of its high mechanical strength and resistance to thermal shock, its ability to be used at high temperatures, its imperviousness to gases, and its excellent electrical properties. However, the properties of alumina ceramics are affected significantly by their composition, microstructure, and sintering temperature and time. Table 1 lists the mechanical, electrical, and thermal properties of several high-alumina ceramics with Al_2O_3 contents ranging from 85 to 100 percent as investigated by Rigterink (ref. 31). LaForge obtained similar results in an earlier investigation and also noted a large variation in the dielectric loss factor among ceramics of the same general type and even of similar composition (ref. 32). Research has also been conducted to determine the effect of various parameters on the ability to produce high-quality ceramic-to-metal seals with high-alumina ceramics. LaForge conducted microscopic studies of alumina ceramics used in ceramic-to-metal seals. He found that the particle size and the sintering temperature had a marked effect on the alumina microstructure and the occurrence of porosity and grain growth. Cole and Hynes examined the properties of an alumina ceramic containing 94.5

percent Al_2O_3 as a function of firing temperature (ref. 33). They noted that stronger ceramic-to-metal seals and lower electrical losses were obtained at higher firing temperatures; however, these favorable properties were obtained at the expense of increased porosity and a lower rupture modulus. Floyd studied the effect of ceramic-flux compositions and crystal size on the strength of ceramic-to-metal joints (ref. 34). These investigations indicated the need for the precise control of each step in the production of alumina ceramic bodies, from analyzing the raw materials to inspecting the finished product. The conclusions apply equally to other ceramic materials.

Several other oxide ceramics have been developed; the most important are discussed below.

1. *Beryllia* (BeO).—In many respects the properties of beryllia are superior to those of alumina; however, beryllia is not nearly so widely used as alumina, probably because of its possible toxicity. The melting temperature of beryllia is about 900°F higher than that of alumina, and its chemical stability surpasses that of most oxides. Beryllia is stable in most gases and in a vacuum at temperatures up to about 3100°F . The heat conductivity of beryllia far exceeds that of all oxide and silicate ceramics; its electrical resistivity is very high as well. Because of its high heat conductivity, beryllia is used in electron tubes where large quantities of heat must be dissipated.

TABLE 1.—*Some Properties of High-Alumina Ceramic Materials*

[From ref. 31]

Material	Percent Al_2O_3	Mechanical		Electrical		Thermal	
		Compressive strength, lb/sq in., 25°C	Tensile strength, lb/sq in., 25°C	Dielectric constant, 1 mc, 25°C	Dissipation factor, 1 mc, 25°C	Coefficient of linear expansion, 25° to 700°C	Softening temperature ($^\circ\text{C}$)
Sapphire (single crystal) -----	100	30×10^4	6.5×10^4	10.3	0.00004	8.5×10^{-6}	2040
Alumina A -----	99+	42×10^4	3.4×10^4	10.0	.0001	8.0×10^{-6}	>1600
Alumina B -----	97	28×10^4	2.7×10^4	9.5	.0001	9.0×10^{-6}	>1600
Alumina C -----	96	30×10^4	2.6×10^4	9.0	.0003	9.0×10^{-6}	>1600
Alumina D -----	94	19×10^4	1.5×10^4	9.2	.0004	7.3×10^{-6}	>1600
Alumina E -----	85	20×10^4	1.8×10^4	8.2	.0009	7.9×10^{-6}	1400

2. *Magnesia* (MgO).—The stability of magnesia in gaseous environments is similar to that of alumina. Magnesia is not as stable as alumina when in contact with most metals at high temperature. It is reduced by carbonaceous atmospheres at elevated temperatures and vaporizes in a vacuum at about 3400°F . Magnesia is not used extensively in vacuum tubes because of its high thermal expansion, poor resistance to thermal shock, and low mechanical strength.

3. *Thoria* (ThO_2).—Thoria is the most stable oxide chemically; it is reducible by the most aggressive alkali metals only under special circumstances. It has the highest melting temperatures of all the oxide ceramics and a correspondingly low vapor pressure. Its use is limited principally by its high cost.

4. *Zirconia* (ZrO_2).—Zirconia is similar to thoria in its chemical stability; however, it is unstable in halogen, sulfurous, and carbonaceous environments. The electrical resistivity and thermal conductivity of zirconia are very low. The poor resistance of zirconia to thermal shock and spalling can be overcome in part by stabilizing zirconia with additions of CaO or MgO .

Additional data on the characteristics and

properties of these and other refractory oxides, such as urania (UO_2) and titania (TiO_2), can be obtained from standard texts on ceramics and from articles by Kingery (ref. 35), McClelland (ref. 36), Schneider (ref. 37), and Ryshkewitch (ref. 38).

In addition to the conventional metal oxides, an impressive number of refractory ceramics have been developed for high-temperature applications. Among these materials are borides, carbides, nitrides, sulfides, and some silicides and aluminides. The properties of these ceramics are not nearly so well documented as those of the metal oxides. As can be seen in figure 1, most of these materials melt at exceptionally high temperatures (ref. 39). Many have excellent oxidation resistance. The properties of some refractory ceramics are shown in table 2 (ref. 40). These materials are used in jet and rocket aircraft, missiles, rockets, and satellites as structural components or coatings to provide oxidation resistance to other structural materials; their uses will increase as their characteristics become better known. Property data on many of these materials were presented at the Asilomar Symposia on high-temperature technology in 1959 and 1963 (refs. 41 and 42). Data

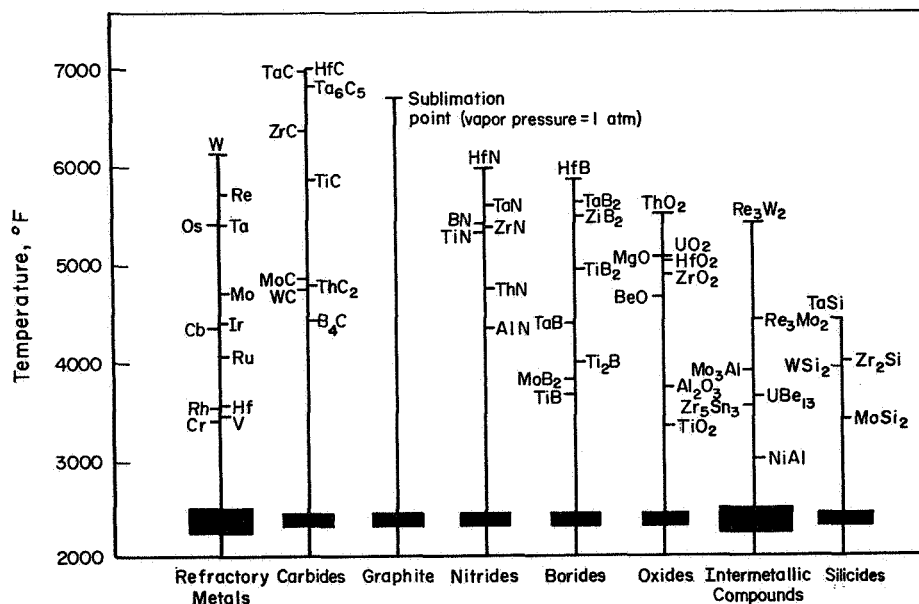


FIGURE 1.—Melting points of refractory materials (ref. 39)

TABLE 2.—*Typical Properties of Selected Refractory Ceramics*^a

[From ref. 40]

Compound	Melting point, °F	Density, gm/cm ³	Knoop hardness (100 gm)	Coefficient of thermal expansion, 10 ⁻⁶ per °F	Thermal conductivity, Btu/hr/ft ² °F	Specific heat, Btu/lb/°F	Electrical resistivity, microhm-cm	Modulus of rupture, 1000 psi	Modulus of elasticity, 10 ⁶ psi	Compressive strength, 1000 psi
OXIDES										
Alumina (Al ₂ O ₃)	3720	3.96	2200.0	8.5 (to 1472)	17.5 (212)	0.36 (1832)	5.0×10 ¹⁵ (ohm-cm)	34.0, 24.0 (1832)	54.0, 46.0 (1832)	450, 40 (2552)
Beryllia (BeO)	4620	3.0	9.0	9.4 (to 2552)	124.0	0.9 (1832)		30.0, 26.0 (1832)	55.0, 49.0 (1832)	110, 30 (2552)
Magnesia (MgO)	5070	3.6	5.5	13.7 (to 2552)	20.4 (212)	0.54 (3092)		23.0, 20.0 (1832)	31.0, 21.0 (1832)	120
Thoria (ThO ₂)	5790	9.7	640.0	9.55 (to 2552)	5.44 (212)			15.0, 15.0 (1832)	35.0, 32.0 (1832)	210, 10 (2552)
Urania (UO ₂)	5200	10.02		1.9 (1832)	0.11 (1832)					
Zirconia (ZrO ₂)	4930	5.6	7.0	5.6 (to 2192)	12.8	0.18 (1832)		20.0, 15.0 (1832)	24.0, 16.5 (1832)	290, 20 (2552)
CARBIDES										
Boron carbide (BN)	4440	2.5	2800.0	4.5 (to 1472)	15.7		0.3-0.8 (ohm-cm)	44.0, 22.0 (1832)	65.0	414
Silicon carbide (SiC)	5160	3.2	2740.0	4.8 (to 1832)	7.9 (2732)	22.3 (1832)	10 ² -10 ³	50.0, 64.0 (2552)	60.0, 40.0 (2696)	120
Hafnium carbide (HfC)	7030	12.7	2900.0	6.3 (to 1202)	12.9	268 (2732)	109.0	35.0, 4.8 (3092)		
Zirconium carbide (ZrC)	5780	6.7	2850.0	6.7 (to 2552)	11.8		70.0	15.0, 2.5 (3632)	69.0, 51.0 (1832)	238
Titanium carbide (TiC)	5700	4.9	3200.0	10.0 (to 3632)	18.2	227 (3012)	190.0	33.0, 13.5 (3632)	64.0	109
Tungsten carbide (WC)	4800	15.8	2100.0	5.0 (to 2552)			53.0	76.0	102.0	
Tantalum carbide (TaC)	7020	14.5	1800.0	6.5 (to 1832)	12.9		30.0	31.0, 17.5 (3632)	55.0	
BORIDES										
Titanium diboride (TiB ₂)	5400	4.5	3370.0	6.39 (to 2462)	15.1 (392)	23.4	15.3	19.0	53.0	97
Zirconium boride (ZrB)	5500	6.1	2300.0	7.5 (to 2462)	13.3 (392)	23.8	9.0-16.0	29.0	64.0	
Tantalum boride (TaB)	5610	12.6	2600.0	5.1 (to 2192)	6.3		68.0			
Molybdenum boride (MoB)	4080	9.31	8.0							
Hafnium boride (HfB)	5880	11.2	2900.0	5.8 (to 2192)	35.9 (1832)		8.0-14.0			
NITRIDES										
Boron nitride (BN)	5430	2.3	230.0	7.7, 7.51 (to 1832)	16.4, 8.9	17.1 (1940)		16.0, 7.3	12.4, 4.9 (77)	45, 34
Aluminum nitride (AlN)	3990	3.3	1225.0	5.64 (to 1832)	17.3 (392), 11.5	17.2 (1112)		38.5, 13.1 (2552)	50.0, 40.0 (2552)	300
Silicon nitride (Si ₃ N ₄)	3450	3.2	9.0	2.5 (to 1832)	8.7			16.0 to 20.0 (77 to 2192)	8.0 (to 1832)	72-90
Titanium nitride (TiN)	5325	5.4	1770.0	9.3 (to 1832)	18.9		130.0, 340.0 (5306)	34.0	11.4	141
Molybdenum disulfide (MoS ₂)	3640	6.24	1260.0	4.5 (to 2600)	18.1 (490), 8.3	0.13 (1800)	75.0-80.0 (2750)	50.0, 13.0 (2750)	58.0, 12.0 (2750)	57-250
Tantalum disulfide (TaS ₂)	4350	9.10	1200.0	4.67 (to 2600)		0.008 (1800)		29.0 (2300), 16.0 (2750)	50.0 (2300), 14.0 (2750)	
Tungsten disulfide (WS ₂)	3960	9.25	1100.0	4.68 (to 2750)	18.0 (1400), 21.0 (2700)	0.008 (1800)		41.0, 45.0 (2750)	43.0, 16.0 (2500)	
Zirconium beryllide (ZrBe ₂)	3500	2.7	1000.0	9.86 (to 2750)	21.0 (1400), 21.0 (2700)	0.41 (1600), 0.47 (2700)	16.1, 100.0 (2300)	25.0, 25.0 (2750)	47.0, 10.0 (2750)	190, 70 (2500)
Tantalum beryllide (TaBe ₂)	3360	4.2	720.0	8.42 (to 2750)	17.7 (1400), 21.7 (2700)	0.28 (1600), 0.30 (2700)	43.5, 138.5 (2300)	31.0, 26.0 (2750)	45.0, 10.0 (2750)	150, 190 (1600)
Molybdenum beryllide (MoBe ₂)	3000	3.0	950.0		18.2 (1600), 17.5 (2600)	0.41 (1600), 0.45 (2600)		42.0 (2300), 13.0 (2750)	15.0 (1600), 1.0 (2750)	

^a Numbers in parentheses are test temperatures in Fahrenheit; values without temperatures are for room temperature tests. ^b Dissociation temperature. ^c Mohs scale. ^d Vickers scale. ^e 500 gm. ^f Perpendicular to grain. ^g Parallel to grain.

are also tabulated in "Refractory Ceramics for Aerospace" by Hague et al. (ref. 43). Current information on the properties and applications of these ceramics is gathered and disseminated by the Defense Ceramics Information Center.

Although much information on the properties and characteristics of various ceramic materials is available, there are many gaps in our knowledge, particularly in regard to their mechanical, thermal, and electrical properties at very high temperatures. As with many materials, property data on ceramics should be accepted cautiously because of the many variables (composition, flux content, impurity level, firing history, and finishing operations) that can affect them. Close cooperation between the ceramic producer and user is recommended for critical applications.

METALS

As in the case of ceramics, the selection of metals for ceramic-to-metal joints or seals largely depends on the specific application. The metals most likely to be used in ceramic-to-metal seals in electron tubes and other vacuum devices are steels of various types, copper and copper alloys, nickel and nickel alloys, and the refractory metals. Several of the precious metals are used also, not usually as structural members because of their cost, but as coatings on contacts and as constituents in brazing filler metals. For other applications it may be necessary to select metals on the basis of corrosion resistance or nuclear properties. Regardless of the application, the metal and ceramic members of the joint must be compatible with the expected service conditions and with each other.

Because of the early demand by the metal fabrication industries, elemental metals and their alloys were produced with lower impurity levels and greater uniformity of properties than ceramics. Also, metal property data are more complete, more readily available, and more reliable than ceramics data.

We will not attempt to summarize the properties of metals used in ceramic-to-metal seals in this report. Such information is available in countless texts and handbooks such as the *Metals Handbook* (American Society for Metals) and Smithell's *Metals Reference Book* (refs. 44 and

45). Hampel has reviewed the properties of many metals used in vacuum tube construction in his *Rare Metals Handbook* (ref. 46); Kohl has done likewise in his *Handbook of Materials and Techniques for Vacuum Devices* (ref. 29). Property data on new structural alloys are available from the manufacturers.

An excellent source of current information on the properties of metals, their fabrication and processing, and their application is the Defense Metals Information Center. This organization gathers data and disseminates them in the form of reports, memoranda, and news releases. Data on most of the metals of interest to the electron-tube industry, with the exception of copper and some of the precious metals, are filed by DMIC. Information on copper can be obtained from the Copper Development Association.

BRAZING FILLER METALS

Since brazing is the most commonly used method of fabricating ceramic-to-metal seals, the process and the filler metals used to complete the joint should be discussed here. Although there are differences in the mechanism of bonding, soldering and brazing have much in common; in both cases, a filler metal that melts at a lower temperature than that of the base metal is required for joining. Because of these similarities, there is some confusion regarding the terms "soldering" and "brazing." The American Welding Society includes an arbitrary temperature restriction in defining the processes; soldering is done at temperatures below 800° F and brazing at temperatures above 800° F. "Silver soldering" and "hard soldering" are terms often used as synonyms for brazing.

Brazing filler metals are selected on the basis of the materials being joined and the expected service conditions. For ceramic-to-metal joint applications, the selection of filler metals is somewhat restricted because most brazing alloys do not wet ceramics easily, but procedures have been developed to overcome this difficulty. The filler metal must be compatible with the base materials and must be capable of meeting the service requirements. For example, it is senseless to select a metal and a ceramic for service in a cesium atmosphere and braze the joint with a

filler metal that does not possess the required corrosion resistance. Similar care must be exercised in selecting joint materials for use in an oxidizing, reducing, or vacuum environment.

Brazing filler metals usually can be grouped according to their major constituent as follows: (1) copper-base alloys, (2) silver-base alloys, (3) nickel-base alloys, (4) alloys based on the noble metals other than silver, and (5) refractory metal-base alloys. The aerospace and nuclear industries require filler metals that maintain their properties at very high tempera-

tures or in very corrosive environments; thus, many experimental alloys based on titanium, zirconium, or the refractory metals have been developed. For the most part, the requirements for ceramic-to-metal joints posed by the electronics industry can be satisfied with filler metals based on copper, silver, or the other noble metals. (The active-metal brazing process, which uses alloys that contain relatively large amounts of titanium or another active metal, is an exception.) Nickel-base alloys are used less frequently than types (1) and (2) because of

TABLE 3.—*Some Commercially Available Noble-Metal Brazing Filler Metals*

[From ref. 47]

Alloy type	Ag	Au	Pd	Cu	Ni	Mn	Cr	Co	Pt	Temperature, °C	
										Solid	Liquid
Ag	100.0									960	960
Ag-Cu	72.0			28.0						780	780
Ag-Cu	50.0			50.0						779	875
Ag-Cu-Ni	77.0			21.0	2.0					779	830
Ag-Cu-Ni	71.5			28.0	0.5					780	795
Ag-Cu-Ni	62.5			32.5	5.0					775	889
Ag-Cu-Ni	71.5			28.0	0.5					780	795
Ag-Cu-Ni-Mn	65.0			28.0	2.0	5				750	850
Ag-Cu-Pd	54.0		25	21.0						901	950
Ag-Cu-Pd	68.0		5	27.0						807	810
Ag-Cu-Pd	58.0		10	32.0						824	854
Ag-Cu-Pd	65.0		15	20.0						850	900
Ag-Pd	95.0		5							970	1010
Ag-Pd	90.0		10							1002	1065
Ag-Pd	80.0		20							1070	1160
Pd-Ni			60		40.0					1238	1238
Ag-Pd-Mn	75.0		20			5				1071	1121
Ag-Pd-Mn	64.0		33			3				1149	1232
Ag-Mn	85.0					15				960	971
Pd-Co			65					35		1230	1235
Au-Cu		94.0		6.0						965	990
Au-Cu		65.0		35.0						1000	1020
Au-Cu		30.0		70.0						1015	1035
Au-Ni		82.0			18.0					950	950
Au-Ag-Cu	20.0	60.0		20.0						835	845
Au-Ag-Cu	5.0	75.0		20.0						885	896
Au-Cu-Ni		81.5		15.5	3.0					900	910
Au-Cu-Ni		35.0		62.0	3.0					990	1025
Au		100.0								1063	1063
Au-Pd		87.0	13							1260	1305
Au-Pd		75.0	25							1380	1410
Pd			100							1552	1552
Pt-Pd-Au		5.0	20						75	1645	1695
Au-Ni-Cr		72.0			22.0		6			974	1065
Pt									100	1769	1769

the reactions that occur between the base metal and filler metal and because of their lower ductility. Table 3 lists filler metals based on the noble metals used in electron-tube construction (ref. 47).

The properties of filler metals and the techniques of brazing are reviewed extensively in the literature (refs. 29, 48 and 49), but several points should be emphasized here. Metals with low-vapor pressures, such as zinc and cadmium, should not be used for ceramic-to-metal joints exposed to a high vacuum. Also, since filler metals are adversely affected by impurities, "vacuum-tube grade" alloys should be specified for critical applications; these are vacuum-

processed alloys in which the impurity content is held to a very low level.

The furnace atmosphere must be considered when ceramic-to-metal joints are brazed, because it affects the base-material properties and the wetting properties of the filler metal. Depending on the materials being joined and the metallizing process used, oxidizing, reducing, or vacuum environments can be used. Titanium and the refractory metals, which are adversely affected by gaseous contaminants, should be brazed in a very good vacuum or in a very pure inert-gas atmosphere. Similar precautions are required when the active-metal process is used for brazing ceramic-to-metal joints.

CHAPTER 3

Ceramic-to-Metal Joint Configurations

To realize the benefits of ceramic-metal structures, it is necessary to use the materials and procedures best suited to their fabrication. Thus, all phases of production from selecting the joint materials to inspecting the finished product must be reviewed in light of the expected service conditions. Some of the variables that must be considered to ensure the reliability of joints and seals will be examined below.

JOINT DESIGN

Selection of Materials

Ceramics

The properties of ceramic materials must be carefully considered and matched against the service requirements, because it is unnecessarily costly to overdesign a ceramic-to-metal structure. For example, the ceramics used for electron-tube envelopes must be dense, vitrified bodies; those used as supports inside tubes need not be so dense and may be slightly porous for ease of outgassing. Larsen suggests three areas of application, each of which emphasizes certain properties which are possessed by ceramics (ref. 50).

1. *Refractory ceramics*.—These ceramics retain their strength and structural integrity at temperatures exceeding 2000° F. They are generally insulators, relatively inert to most environments, and resistant to many molten metals and fused salts. Ceramics of this type can withstand high, steady-state temperatures indefinitely; however, the build-up of thermal stresses resulting from excessive thermal shocks can produce cracking. Ceramics with low elastic moduli, low thermal expansion coefficients, and

high heat conductivities are usually resistant to thermal shocks; they are used as structural members or metal coatings to provide oxidation resistance.

2. *Electrical ceramics*.—These ceramics are characterized by their high resistivity, low dielectric losses, and high breakdown voltage. They are used for high-temperature applications where structural integrity is important along with excellent electrical properties. Hard glasses and mica can also be used as electrical insulators; however, the usefulness of these materials is limited by their service temperatures—about 1000° F for glasses and 1500° F for mica.

3. *Mechanical ceramics*.—The usefulness of these ceramics is governed by their strength, hardness, creep resistance, and chemical inertness at high temperatures. Included among these materials are the metal-bonded carbides and ceramic-metal combinations, also known as cermets.

Other properties of ceramics that may be of importance, depending on the service requirements, are surface finish, porosity, uniformity of density, vacuum tightness, freedom from internal strains, transparency, and machinability.

Larsen has suggested the use of a chart (table 4) that lists the refractory, electrical, and mechanical properties of many available ceramic bodies. Knowing the service requirements, it is a relatively simple procedure to select the ceramics that most nearly meet these requirements. When two or more ceramic materials appear to be suitable, final selection may be based on other considerations such as cost, availability, and ease of fabrication.

TABLE 4.—*Properties of Ceramics*

[From

	REFRACTORY								
	Silicon carbide (ceramic-bonded)	Silicon carbide (silicon nitride-bonded)	Mullite (synthetic) (3Al ₂ O ₃ ·2SiO ₂)	Thoria (ThO ₂)	Magnesia (MgO)	Zirconia (stabilized) (ZrO ₂ -2% CaO)	Fused silica (SiO ₂)	Pyroceram (9605)	Hard glass
PHYSICAL PROPERTIES									
Melting or softening temp., ° F.....	3500	3540	3320	5830	5070	4710	3050	2460	-----
Max. use temperature, ° F.....	3200	3000	3000	4890	4170	4600	2700	1300	1300
Specific gravity.....	2.6	2.9	2.6	10.5	3.6	6.1	2.2	2.6	2.4
Thermal conductivity Btu/sq ft/hr/° F/in.:									
at RT to 212° F.....	-----	-----	-----	73	240	14	9.5	2.4	4.0
at 1000° to 1100° F.....	-----	-----	-----	23	84	14	-----	-----	-----
at 1830° F.....	-----	-----	-----	20	49	17	-----	-----	-----
at 2200° F.....	109	114	15	-----	-----	7	-----	-----	-----
Expansion coefficient, micron/in./° F:									
at RT.....	-----	-----	-----	-----	-----	-----	-----	-----	-----
RT to 570° F.....	-----	-----	-----	-----	-----	-----	0.56	7.7	-----
RT to 930° F.....	-----	-----	-----	5.0	-----	-----	-----	-----	-----
RT to 1470° F.....	-----	-----	-----	-----	7.5	-----	-----	-----	-----
RT to 2600° F.....	2.4	2.4	2.5	-----	-----	3.1	-----	-----	-----
Thermal shock resistance.....	fair	good	good	poor	poor	fair	excellent	excellent	good
ELECTRICAL PROPERTIES									
Dielectric strength, v/mil at RT.....	-----	-----	300	-----	-----	-----	-----	300	350
Dielectric constant at 1 mc at RT.....	-----	-----	7.0	-----	-----	-----	3.8	6.1	4.0-14
Resistivity, ohm-cm:									
at RT to 212° F.....	-----	-----	10 ¹⁵	-----	-----	-----	10 ¹⁷	10 ¹³	10 ¹⁷
at 570° F.....	-----	-----	-----	-----	-----	-----	-----	-----	-----
at 900° F.....	-----	-----	-----	-----	-----	-----	-----	-----	-----
at 1500° F.....	-----	-----	10 ⁸	-----	10 ⁹	-----	-----	-----	-----
at 2200° to 2300° F.....	-----	-----	-----	2×10 ⁴	8×10 ¹¹	32	-----	-----	-----
MECHANICAL PROPERTIES									
Flexural strength, psi×1000 at RT.....	2.2	5.6	0.5	-----	-----	27	15	37	15
		(at 2460° F)	(at 2460° F)	-----	-----	-----	-----	-----	-----
Tensile strength, psi×1000 at RT.....	low	3	18	-----	-----	-----	-----	20	8
Compressive strength, psi×1000:									
at RT.....	15	20	150	214	-----	300	-----	-----	100
at 590° F.....	-----	-----	-----	71	-----	-----	-----	-----	-----
at 2200° F.....	-----	-----	-----	28	-----	114	-----	-----	-----
Modulus of elasticity, psi.....	13.2	17	-----	21	12	32	10.5	19.8	100
Hardness:									
Mohs.....	9	9.6	6-7	-----	6	7	-----	-----	700
Knoop.....	2500	-----	-----	-----	-----	1100	-----	1100.0	-----
Charpy impact strength, in.-lb.....	-----	-----	-----	-----	-----	-----	-----	-----	1.2
Abrasion resistance.....	excellent	excellent	fair	fair	poor	fair	good	good	good

a 72° to 390° F.

b 390° to 930° F.

c 930° to 1470° F.

d 1430° to 2190° F.

e 72° to 1830° F.

and Application Classifications

ref. 50]

ELECTRICAL							MECHANICAL				
Alumina (98% Al ₂ O ₃)	Alumina (99.5% Al ₂ O ₃)	Beryllia (dense) (BeO)	Steatite (MgO· SiO ₂)	Cordierite (2MgO· 2Al ₂ O ₃ · 5SiO ₂)	Forsterite (2MgO· SiO ₂)	Lithia porcelain	Titanium carbide (cobalt- bonded)	Tungsten carbide	Boron carbide	Zirconium carbide	Silicon nitride
3700	3700	4650	2550	2610	2620	-----	5680	5031	4080	6390	3450
3000	3180	3600	1830	2280	1800	1800	2800	4700	3500	-----	2800
3.7	3.8	3.0	2.7	2.1	2.9	2.3	5.5-6.5	12-16	2.5	6.2	3.4
200	217	1460	17.4	8.7	24	14.4	120	64	-----	145	130
64	-----	325	-----	-----	-----	-----	-----	-----	-----	-----	-----
43	59	174	-----	-----	10.3	-----	-----	-----	188	-----	-----
-----	-----	170	-----	-----	-----	-----	-----	-----	-----	-----	-----
-----	a 3.8	-----	-----	-----	-----	-----	4.3-5.8	-----	-----	-----	3.1
-----	b 4.4	4.0	4.5	1.2	-----	-----	4.5-6.0	2.5-4	-----	3.5	-----
4.0	c 4.9	5.0	5.0	-----	-----	-----	-----	-----	-----	-----	-----
-----	d 5.4	-----	-----	-----	6.1	-----	-----	-----	1.7	-----	-----
-----	e 4.7	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
good	good	excellent	poor	fair	fair	good	good	fair	poor	poor	good
300	330	300	220	100	240	250	Carbides generally exhibit electrical semiconductor properties.				
8.9	9.7	7.0	5.9	5.0	6.2	5.6					
-----	-----	10 ¹⁴	-----	-----	1.8×10 ¹²	-----					
-----	1.5×10 ¹¹	8.0×10 ¹³	-----	-----	-----	-----					
1.0×10 ¹⁵	1.4×10 ⁹	-----	12.0×10 ¹⁰	5.0×10 ¹⁰	-----	-----					
-----	-----	-----	-----	-----	3.0×10 ⁵	-----					
1.0×10 ⁵	-----	3.0×10 ¹²	-----	-----	-----	-----					
-----	-----	-----	-----	-----	-----	-----					
40	46	26	21	8.0	20	8.0	-----	80	44	5	34
30	-----	18.5	10	3.5	10	1.5-3.5	26-134	130	22.5	(at 2730° F) 14.4	15.8
300	300	114	90	30	85	60.0	265-450	500-800	414	238	-----
185	-----	92	-----	-----	-----	-----	-----	-----	-----	-----	-----
71	-----	34	-----	-----	-----	-----	-----	-----	-----	-----	-----
40	52	45	7.5	7	-----	120.0	42-57	102	62	45	42
9	-----	9	-----	7	7.5	7.5	-----	-----	9.3	8.9	-----
1750	-----	1500	-----	-----	-----	1400.0	1400-1800	1880	2800	-----	2090
7	-----	-----	5.0	2.5	4.0	3.0	18-192	-----	-----	-----	-----
excellent	excellent	good	fair	fair	good	good	excellent	excellent	excellent	excellent	good

Metals

As in the case of ceramics, the metals for ceramic-to-metal joints and seals are selected primarily on the basis of the service requirements. The most commonly used metals are low-alloy, medium-alloy, and stainless steel; copper and copper alloys; nickel and nickel alloys; and refractory metals and alloys. Several of the noble metals are used in ceramic-to-metal joints; however, because of their high cost they are usually used as constituents in brazing filler metals rather than as structural members. Other metals may be used to meet a specific requirement, such as resistance to liquid metals and low nuclear cross section.

A chart similar to table 4 could also be prepared to aid in selecting metals for ceramic-to-metal joints and matching the service requirements to the physical, mechanical, and electrical properties of the respective metals. The number of alloys included in each classification, however, would expand the chart excessively.

The selection of the metal member of a joint is governed somewhat by the physical and electrical service requirements but even more by the ceramic used. Characteristics such as magnetic properties, electrical conductivity, and strength determine the selection of a group of metals; final alloy selection is based on the degree to which the linear-expansion coefficients for the metal and ceramic can be matched.

Joint Design and Configuration

The joint configurations that can be used for ceramic-to-metal seals and joints are more limited than those for joining metals because of the need to join materials with differing properties. This problem is similar to that encountered in joining dissimilar metals not metallurgically compatible. However, in this instance we are primarily concerned with eliminating or minimizing stresses resulting from the different expansion coefficients of the joint members.

Ceramics are inherently brittle materials, much stronger in compression than in tension; in comparison to most metals, they have small expansion coefficients. Ideally, the ceramic and metal selected should have identical expansion

coefficients over a wide temperature range and without hysteresis, so that these materials can expand and contract at equal rates throughout the joining and operating cycle. Figures 2 and 3 show that this is not the case. As a result, ceramic-to-metal joints must be carefully designed to emphasize the advantages and minimize the disadvantages of each material.

Different expansion coefficients are primarily responsible for introducing stresses into a ceramic-metal structure, but other problems can be created as well. If, for example, Kovar is brazed to a 96-percent alumina body, both ma-

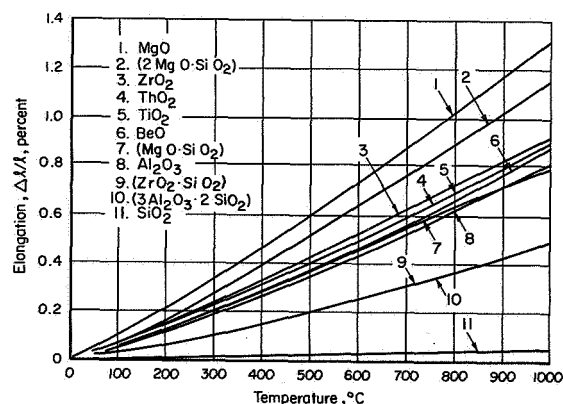


FIGURE 2.—Thermal expansion characteristics of ceramic materials

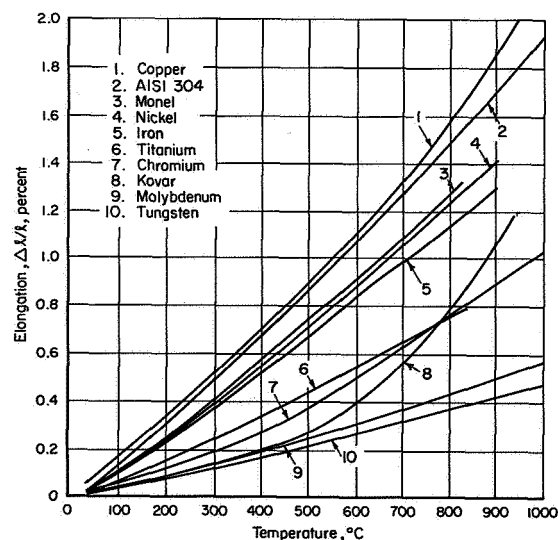


FIGURE 3.—Thermal expansion characteristics of metals used in ceramic-to-metal joints

materials expand at the same rate up to about 450° C, as shown in fig. 4 (ref. 51). Above this temperature, Kovar expands faster than alumina. Thus, a Kovar ring located inside a ceramic ring will produce compressive stresses in the ceramic body at temperatures above 450° C; these stresses can be eliminated if the position of the rings is reversed. However, with the parts reversed, the clearance between the Kovar and ceramic rings increases as the temperature rises, and problems in brazing can occur. When silver-base alloys are used for brazing, the recommended joint clearance is 0.003 to 0.005 inch; however, the clearance for joints brazed with copper ranges from a press fit to about 0.001 inch. A filler metal with sluggish flow characteristics is recommended for brazing joints where large clearances between joint members are expected. Furthermore, the filler metal should be ductile enough to withstand the stresses produced as the joint members contract during the cooling cycle.

Most of the ceramic-to-metal seal configurations have been designed for electron-tube application; however, many of the designs are equally

suitable for other applications. Although some of the seal designs appear complicated, they are composed of basic types, such as the butt seal, lap seal, pin seal, and disk seal. In addition, many types of flexible seals have been developed to accommodate joint members with different expansion coefficients. Special designs have been prepared to join ceramic bodies to massive metal members that cannot flex during the joining or operating cycles; thin metal transition sections have proved useful in such cases. Several typical joint designs are shown in figure 5 (ref. 52); other designs are available in the technical literature.

Several investigators have conducted stress analyses to optimize seal design, indicate areas of high stress concentrations, and provide criteria for designing seals of different sizes (refs. 53 to 55). In a typical study, Cole and Inge derived mathematical expressions to predict the unit stress at the interface of a ceramic-to-metal seal, measured the residual stresses on the outside of the metal member of a ceramic-to-metal seal with strain gauges, and compared calculations of the predicted and measured stresses on the outer surface of the metal member (ref. 53). Using ceramic-to-nickel and ceramic-to-stainless-steel seals, Cole and Inge found the predicted stress to be about 30 percent higher than the measured stress; apparently, the major source of error was to ignore the possible filler-metal effects on the seal stresses. Mark and Lewin analyzed the stresses that were present in ceramic-to-metal butt and disk seals (ref. 55). The theoretical studies were supported by strain gauge measurements and three-dimensional photoelastic model analysis.

SURFACE PREPARATION

Machining (Grinding)

The ceramic bodies for ceramic-to-metal seals may be produced by extrusion, slip casting, dry- or wet-pressing, isostatic pressing, injection molding, and hot compacting. Ceramics designed for metallized assemblies should have smooth contours and simple shapes; sharp edges and corners should be avoided to eliminate concentration of stress. Whenever possible, ceramic bodies should be designed with generous toler-

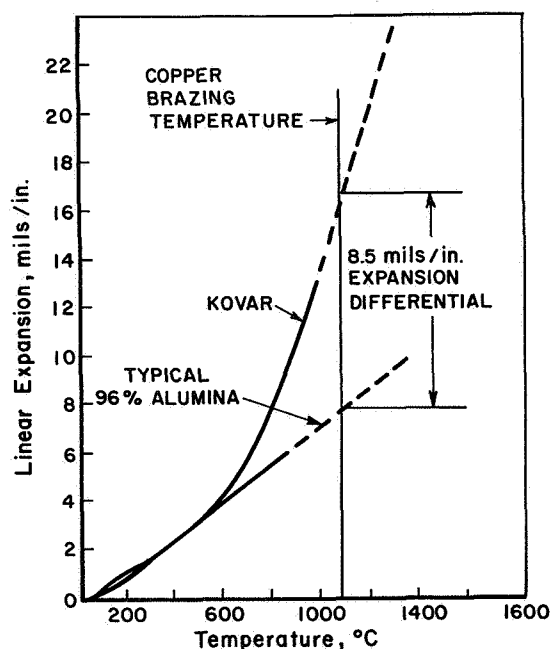


FIGURE 4.—Thermal expansion characteristics of Kovar and alumina (ref. 51)

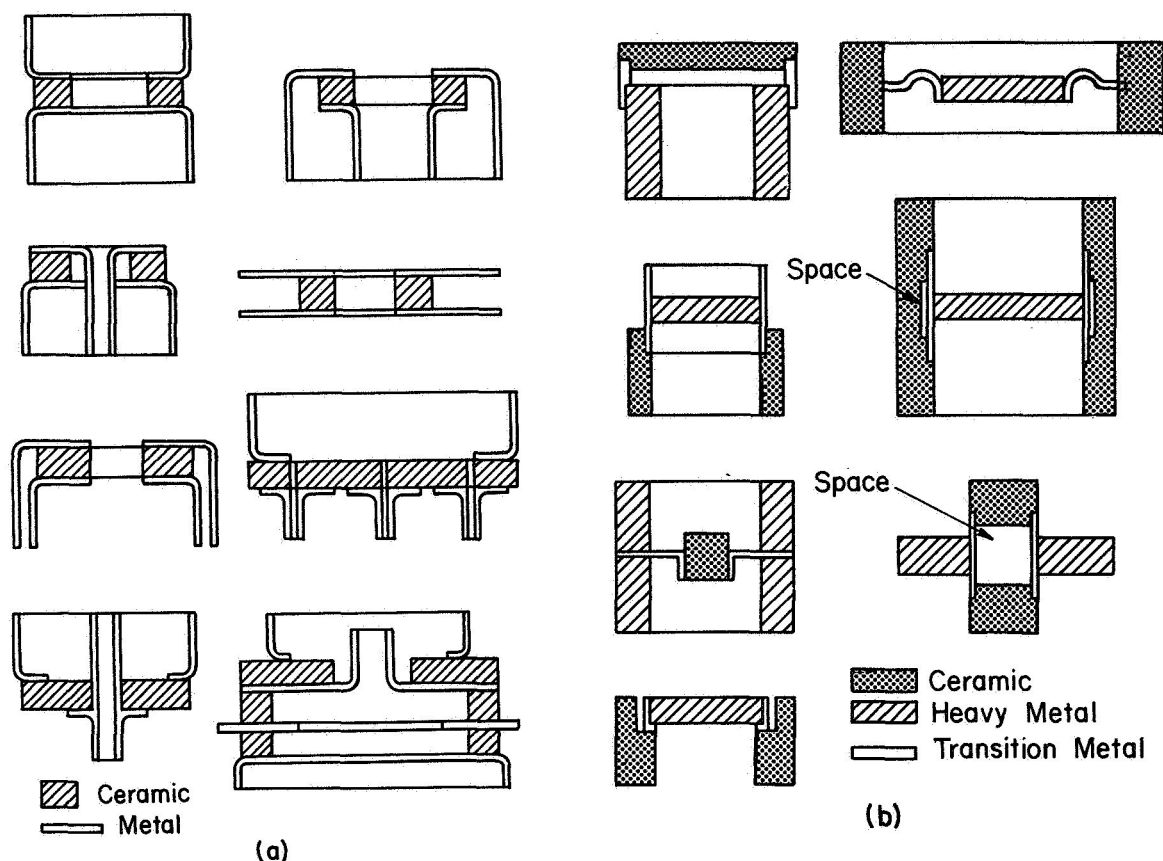


FIGURE 5.—Ceramic-to-metal joint configurations (ref. 52). (a) Butt and lap seal joint designs; (b) joint

designs for transitions to thick all-metal members; (c) backup of ductile metal seal with blank ceramic

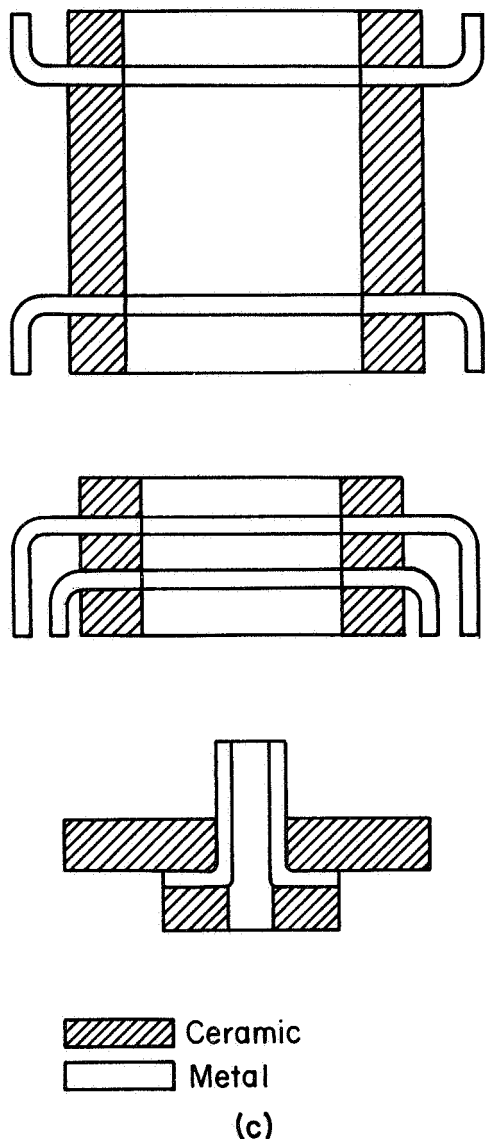
ances to permit their production without subsequent grinding. Ceramics can be produced in commercial quantities with tolerances of about ± 0.005 inch on dimensions up to 0.50 inch and about ± 1 percent on larger dimensions. Because diamond-cutting abrasives must be used, grinding is costly even where the surfaces are accessible; costs are prohibitive when less readily accessible surfaces must be finished. In addition, grinding may introduce macrocracks that act as stress risers or notches, as well as stresses that are difficult or impossible to detect. Such stresses can result in excessive brazing clearances and highly stressed joints during the joining or operation cycles.

Despite the disadvantages of grinding, ceramic components used in vacuum-tube construction must often be ground to closer toler-

ances than those to which they can be formed, because the location and spacing of internal structural members are critical to performance. Janssen has discussed the equipment and grinding techniques used to produce precision ceramic bodies (ref. 56).

Cleaning

The cleaning of ceramic surfaces before metallizing and joining is an essential step in the production of reliable ceramic-to-metal seals. As received from the producer, the surfaces of ceramic bodies may be contaminated by organic substances such as traces of oil or grease, fingerprints, and films of adsorbed gases; occasionally, metallic contaminants may also be present. During sintering operations,



oily substances are reduced to carbon, and metals are converted to oxides; these materials can prevent consistent metallizing and bonding. In addition, they stain the ceramic surface and may cause sparking, electrical leakage, and radio-frequency losses.

Many procedures and techniques have been developed for cleaning ceramic surfaces, depending on the particular ceramic. Loosely adhering particles can be removed by scrubbing the ceramic surface with a water paste of alu-

mina grit; then, the ceramic body is rinsed in water and acetone and air-dried. Small ceramic parts can also be ball-milled to remove contaminants. As a second step, Johnson and Cheatham recommend that the parts be boiled in clean, concentrated nitric acid for 30 minutes, rinsed in distilled or deionized water, boiled in deionized water for 10 minutes, and rinsed again (ref. 52). Following this treatment, the ceramic parts are given a final rinse in methanol and air-dried at 120° C (248° F).^{*} Then, the parts are fired in air at 1000° ± 25° C (1832° ± 45° F) for about 10 minutes, cooled, and placed in clean polyethylene bags. Slow heating and cooling rates are used to minimize thermal shocks. Metallizing should be undertaken within 3 days after cleaning.

Other methods using alkaline rinses rather than nitric-acid treatments have also been used to clean ceramic surfaces. The bombardment of ceramic surfaces with gaseous ions to remove surface contaminants has been discussed by Bierlein, Newkirk, and Mastel (ref. 57). This technique has been used to remove oxides and other contaminants from metallic surfaces for critical applications.

After cleaning, the ceramic bodies must be handled carefully with lint-free gloves to prevent recontamination of their surfaces; tweezers, spatulas, and other tools must be plastic-coated or made from nonmetallic materials.

Oxides and other surface contaminants should be removed from the metals used in ceramic-to-metal seals with the same care reserved for ceramics. Johnson and Cheatham recommend the following procedure to clean nickel, Monel, Kovar, and stainless-steel surfaces: Ultrasonically clean the parts in trichloroethylene and rinse in hot water; etch the metals in concentrated hydrochloric acid; and rinse the parts in cold tap water and then in cold, deionized water (ref. 52). The metal parts are then dipped in methanol and air-dried at 120° C. Other

^{*}Both Centigrade and Fahrenheit temperatures are given in this report. The first figure is the temperature cited by the author; the second figure is the converted value of the original data.

etchants for these metals can be found in standard references on metals.

Metallizing

The first ceramic-to-metal joints were successfully produced by brazing a metallized ceramic to a metal member with a silver-base filler metal in the 1930's. Despite the advances in joining technology since then, this is still the most extensively used method of fabricating such joints. Of course, significant improvements in the techniques of metallizing have been made and several new procedures have been developed and evaluated. Also, extensive research on the reactions that occur when a ceramic surface is metallized has contributed to the effectiveness of metallizing.

Metallizing procedures were originally developed to improve the wettability of ceramic surfaces by conventional low-temperature filler metals. Later investigators found that some active metals and their alloys or compounds (e.g., titanium and zirconium) would wet unmetallized ceramic surfaces under certain conditions. Although variations of the so-called active-metal process have been used commercially to produce ceramic-to-metal seals, they have not been accepted to the extent characterized by the metallizing-brazing concept of joining these materials.

In reviewing developments in this area, it should be emphasized that metallizing is a surface preparation for ceramics, not a joining process. While most metallized ceramics are joined to metals by brazing, other processes such as diffusion, pressure, and ultrasonic welding have been used also.

Sintered Metal Powder Processes

These metallizing processes are based on the work of Vatter and Pulfrich in the 1930's and have one common feature, i.e., the metallizing coating is sintered to the ceramic surface. Vatter and Pulfrich mixed finely divided metal powders (molybdenum, tungsten, rhenium, iron, nickel, or chromium) with a suitable binder to form a suspension that was painted on the ceramic surface to be metallized. Then the coat-

ing was sintered to the ceramic at a high temperature. Pulfrich used a controlled hydrogen atmosphere for sintering while Vatter used a vacuum. While the desirability of adding certain metal oxides to the final metal powders as a means to improve adhesion between the powder coating and the metal was recognized, Nolte and Spurck are credited with these improvements (refs. 58 and 59).

In 1950, Nolte and Spurck described a procedure to metallize ceramic surfaces with molybdenum at temperatures as low as 1250° C (2282° F). The metallizing mixture was prepared by ball-milling the following ingredients for 24 hours:

- 160g molybdenum powder (200 mesh)
- 40g manganese powder (150 mesh)
- 100cc pyroxylin binder
- 50cc amylacetate
- 50cc acetone.

After ball-milling, the mixture was thinned to the proper consistency for painting or spraying, and a 0.001- to 0.002-inch coating was applied to the ceramic surface. Then the coated ceramic was fired in a hydrogen atmosphere for ½ hour at 1350° C (2462° F). Nolte and Spurck recommended a sintering temperature of 1350° C for a metallizing mixture that contained 20-percent manganese; however, satisfactory metallizing was observed when the manganese content was reduced to 10 percent or when the sintering temperature was decreased to 1250° C (2282° F).

The process developed by Nolte and Spurck is known as the "moly-manganese" process. It has been widely accepted by industry as a standard method to metallize ceramic surfaces, and numerous variations have been developed to extend the usefulness of the process. For small production runs and oddly shaped bodies, the metallizing mixture is usually applied with a small brush; care must be observed to apply the coating evenly. Spray-coating, roller-coating, and silk-screening require more elaborate equipment and are thus suitable for large production runs. The metallizing mixture can be supplied on transfer tape for application to the ceramic surfaces (refs. 60 and 61). In producing this tape, the metallizing mixture is spread uni-

formly on a polyethylene sheet and coated with a pressure-sensitive adhesive that is protected by a paper during shipment and storage. To use, the protective paper is removed and the ceramic bodies are pressed onto the tape; when the ceramic is lifted from the tape, the metallizing coating is transferred to the part. Sintering is done in the usual manner. Standard metallizing coatings can be supplied on transfer tape or proprietary coatings can be ordered. Industry has highly automated tape-transfer operations as well as other methods of applying metallizing mixtures to ceramic bodies.

Engineers at the Sperry Gyroscope Company conducted an extensive program to improve the reliability of the sintered metal powder metallizing process (ref. 53). Starting with a review of the literature, the researchers analyzed the observations and theories of adhesion between the metallizing coating and the ceramic body to determine the classes of materials that appeared to promote adhesion; additional theories on adhesion were also proposed. Based on this analytical approach, over 200 metallizing mixtures were formulated and evaluated. Each mixture was applied to ceramic bodies containing 94.0-, 96.0-, and 99.6-percent alumina; sintering was done at three temperatures between 1250° and 1700° C (2282° and 3092° F). The metallizing powders were mixed with a binder of acetone, amylacetate, and nitrocellulose lacquer and ball-milled for 24 hours. The effectiveness of metallizing was determined by tests that measured adherence, peel strength, compressive strength, and tensile strength; approximately 3200 specimens were prepared and evaluated. The tests indicated that many metals and oxides can be used in place of manganese; at least 16 metallizing mixtures produced seals with equal or greater strength than those produced by the moly-manganese process. The compositions of seven of the most promising mixtures are shown in table 5 along with the processing and test data. The workers at Sperry concluded that:

1. The tensile strength of ceramic-to-metal seals made with the three alumina bodies decreased with increasing alumina content. The maximum tensile strengths were 28 400, 22 000, and 16 100 psi for the 94.0-, 96.0-, and 99.6-percent alumina ceramics, respectively.

2. The optimum sintering temperatures were 1500° to 1600° C (2732° to 2912° F).

3. Metallizing mixtures for the 99.6-percent alumina body invariably required additions of silica or silicate-bearing minerals to produce satisfactory seals.

Other metallizing compositions have been cited by Kohl and Rice (ref. 62) and LaForge (ref. 63). These are basic molybdenum-manganese mixtures with additions of titanium hydride, iron, and various metal oxides to promote adhesion of the metallizing layer to the ceramic surface.

In 1966, the Sperry Electronic Tube Division concluded a program to develop low-temperature metallizing materials (ref. 64). It is known that the microstructure and properties of ceramics change significantly when heated to the high temperatures required to sinter moly-manganese coatings. For example, Cole and Hynes (ref. 33) noted that the seal strength increased at the expense of the modulus of rupture, apparent porosity, and apparent density when the firing temperature exceeded 1550° C (2822° F). Tentarelli, White, and Buck observed sizable increases in the physical dimensions of a 94-percent alumina body when it was heated to temperatures above 1475° C (2687° F). Others have reported increases as high as 1.4 percent in the length of a 96-percent alumina ceramic heated above 1475° C. Such variations in physical dimensions do not occur at lower firing temperatures in the 900° to 1100° C (1652° to 2012° F) range. The stability of ceramics is critical in electronic assemblies where performance depends on close tolerances.

The engineers at Sperry formulated a series of metallizing paints based on metal oxides of molybdenum, manganese, and tungsten. While molybdenum has received the most attention as a metallizing constituent, tungsten has also been investigated to metallize ceramics for high-temperature service (ref. 65). A statistical analysis was made to evaluate two paints, as shown in tables 6 and 7 at 900°, 1000°, and 1100° C (1652°, 1832°, and 2012° F), and coating thicknesses of 0.005, 0.010, 0.015, and 0.020 inch. The metallizing paint was applied to alumina ASTM test pieces (fig. 6) in the desired thickness; then, the coating was sintered to the ce-

TABLE 5.—*Metallizing Compositions*

[From ref. 53]

Composition Number	Composition and weight, g	Sintering temperature, °C	Ceramic, percent Al ₂ O ₃	Peel test values, in.-lb	Compression values, lb	Tensile test values, psi
65	292.5 Mo-----	1500	94. 0	2. 5	>4000	28400
	7.5 Ti-----				>4000	19350
					>4000	16400
91	270 Mo-----	1500	94. 0	2	>4000	15500
	30 LiMnO ₃ -----				>4000	15700
					3300	14500
141	291 Mo-----	1600	94. 0	4	3700	12300
	9 Talc-----				3400	17900
	(MgO-SiO ₂)-----				3900	16100
72	240 Mo-----	1500	96. 0	2	3800	9430
	73.6 CeO ₂ -----				3600	22000
					4000	16050
50	255 Mo-----	1300	96. 0	2	2800	15700
	48 SiO ₂ -----				3000	13200
	22 Mn-----				3800	10700
50	255 Mo-----	1500	99. 6	2	2200	14000
	48 SiO ₂ -----				2300	16100
	22 Mn-----				1600	15200
49	255 Mo-----	1500	99. 6	2. 75	>4000	11300
	48 SiO ₂ -----				3500	11600
	26 MnO-----				1200	16100

ramic surface in an atmosphere of dissociated ammonia. To evaluate the quality of the metallizing treatment, pairs of the ASTM pieces were brazed with copper and tested in tension. Tentarelli et al. observed that:

1. There were no essential differences in seal strength, regardless of the metallizing temperature or coating thickness.

2. Average tensile strengths of 13 000 to 14 000 psi were obtained with various alumina ceramics, and strengths of 11 300 psi were obtained with beryllia bodies.

3. Thermal-cycling tests were used to evaluate the seal reliability obtained with the MoO₃/MnO₂ low-temperature metallizing system relative to the reliability obtained with conventional high-temperature Mo/Mn systems; no significant differences in the results were noted.

TABLE 6.—*Evaluation of MoO₃/MnO₂ Metallizing Paint**

[From ref. 64]

Metallizing thickness, inches	Tensile strength, psi at indicated reduction temperature		
	900° C	1000° C	1100° C
0.0005	10 300	8 300	10 800
	11 200	10 000	9 900
0.0010	10 900	11 400	7 100
	10 100	9 000	10 100
0.0015	11 100	7 900	5 800
	10 000	11 200	9 400
0.0020	11 600	9 800	9 400
	12 200	13 100	10 500

*Metallized film was 95Mo-5Mn.

TABLE 7.—*Evaluation of $WO_3/MnO_2/Fe_2O_3$ Metallizing Paint**

[From ref. 64]

Metallizing thickness, inches	Tensile strength, psi at indicated sintering temperature			
	800° C	900° C	1000° C	1100° C
0.0004	9 700	10 900	10 200	12 900
to	5 500	7 600	14 500	9 800
0.0007	6 600	5 200	17 000	13 300
	9 400	4 700	6 300	3 400
0.0008	5 800	10 400	7 200	11 500
to	15 100	4 700	6 500	10 500
0.0012	11 900	5 700	9 100	8 400
	11 200	6 600	11 100	7 700
0.0013	7 200	3 900	11 100	4 100
to	9 500	13 700	13 200	13 200
0.0017	5 400	6 400	3 300	8 400
	3 700	9 100	3 600	9 600
0.0018	5 600	10 800	7 900	5 100
to	3 700	7 600	6 900	3 700
0.0023	4 600	9 000	6 900	6 900
	3 100	7 300	3 900	8 900

*Metallized film was 94W-5Mn-1Fe.

4. The low-temperature metallizing systems were suited for silk-screen and transfer-tape methods of application. Compared with the moly-manganese process, low-temperature metallizing offers economic advantages associated with lower sintering temperatures and less critical sintering atmospheres.

In a program to develop ceramic-to-metal seals for nuclear thermionic energy converters, Bristow, Grossman, and Kaznoff investigated metallizing systems to prepare essentially pure-alumina ceramic surfaces for brazing (ref. 11). In the conventional moly-manganese process, the manganese is oxidized during the metallizing operation and reacts with (1) the alumina body itself to form manganese alumina compounds, and (2) the fluxing oxides in the ceramic to form a glassy phase that locks the molybdenum coating to the ceramic surface. However, the seal strength tends to decrease as the alumina content of the ceramic increases, presumably because less fluxing oxides are present. For this application, silica-free

alumina ceramics were required for a high-temperature cesium-vapor environment, and the fluxing oxides had to be incorporated in the metallizing mixtures. The composition of the experimental metallizing materials was 60- to 70-volume percent molybdenum powder plus 30- to 40-volume percent fluxing oxides of aluminum, calcium, magnesium, barium, or yttrium (table 8). The powder mixtures were dispersed in an organic binder and ball-milled for 144 hours. After mixing, the metallizing suspensions were thinned to the proper consistency and applied to the ceramic surfaces by silk-screen techniques. The coated ceramics were then sintered at various temperatures in a dry-hydrogen atmosphere. The quality of metallizing was evaluated by preparing and leak-testing ceramic-to-metal seals; these data are summarized also in table 8. Satisfactory seals were obtained with ceramics that were metallized at relatively high temperatures. Similar procedures to metallize high-purity alumina ceramics were developed by

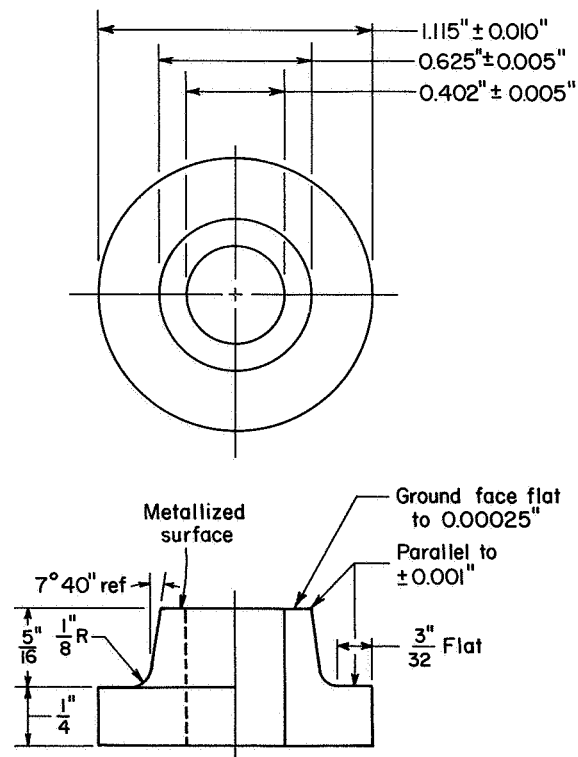


FIGURE 6.—ASTM tensile test piece (ref. 82)

TABLE 8.—*Composition of Metallizing Materials and Results of Sealing Studies*

[From ref. 11]

Metallizing		Oxide constituents, w/o					Sintering temperature, ° C	Leak check results	
Mix Number	Oxide composition Number	Al ₂ O ₃	CaO	MgO	BaO	Y ₂ O ₃		Vacuum tight	Leakers
1	26	51.8	41.5	6.7	-----	-----	1610	0	6
							1680	0	6
							1750	3	1
							1755	5	1
							1760	3	0
							1800	3	0
							1850	7	0
18	20	80.0	17.0	3.0	-----	-----	1700	0	3
							1750	0	3
							1800	0	6
							1850	3	0
							1900	3	0
21	47	95.0	4.3	7.0	-----	-----	1700	0	2
							1750	0	3
							1800	3	3
							1850	1	2
							1900	0	3
36	48	80.0	20.0	-----	-----	-----	1700	0	3
							1750	0	3
							1800	1	5
							1850	3	0
							1900	3	0
54	44	60.0	-----	-----	40	-----	1750	0	3
55	46	65.0	-----	-----	-----	35	1800	3	0
							1850	2	1
							1900	3	0

Klomp and Botden (ref. 66). Molybdenum powder was added to mixtures of CaO, Al₂O₃, SiO₂, and MgO in the following proportions: 80-weight percent molybdenum plus 20-weight percent oxide powder.

Many investigators have discussed the importance of powder-particle size in metallizing mixtures. It is generally agreed that the size of the particles should be about 1 to 8 microns in diameter; however, fine and coarse particles must be blended to produce metallizing paints

with the required viscosity and surface tension. The method used to apply the paint to the ceramic surfaces also has a significant bearing on the particle size and distribution.

Reactive- or Refractory-Metal Salt Coating

Ceramics can also be metallized by painting them with a solution of a refractory-metal salt. The ceramic is then dried and sintered to reduce the metal salt to a metal that bonds to the

ceramic, leaving a thin, adherent metal coating on the surface of the ceramic. The ceramic bodies can also be immersed in the solution, but then the sintered metal coating must be ground off areas requiring insulation. In a program to develop low-temperature metallizing procedures, Tentarelli, White, and Buck investigated the use of water-soluble refractory-metal salt for metallizing (ref. 64). The metal salts were dissolved in an appropriate amount of

water. Then the solution was painted on alumina ASTM test pieces that were preheated to facilitate drying. After drying, the coated ceramic pieces were heated to 1100° C (2012° F) in a dissociated-ammonia atmosphere whose dew point was 5° C (41° F). The ASTM test pieces were brazed in pairs with copper, and the assemblies were tested in tension to evaluate the metallizing procedure. Table 9 presents the composition of the experimental metallizing solutions along

TABLE 9.—*Evaluation of Low-Temperature Solution-Metallizing Paints*

[From ref. 64]

Composition of metallizing paint	Ceramic, percent Al ₂ O ₃	Average RT tensile strength, psi
4.2g ammonium molybdate.....	94.0	12 600
0.2g potassium permanganate.....		
18.7g sodium molybdate.....	94.0	10 050
0.2g potassium permanganate.....		
2.4g ammonium molybdate.....	94.0	7 300
0.2g lithium molybdate.....		
0.05g potassium permanganate.....		
24.0g ammonium molybdate.....	94.0	14 000
0.2g potassium permanganate.....		
60.0g ammonium molybdate.....	94.0	3 500
3.0g ferrous ammonium sulfate.....		
25.0g ammonium molybdate.....	94.0	12 600
0.2g ferrous ammonium sulfate.....		
30.0g ammonium molybdate.....	94.0	13 300
0.5 ml manganese nitrate (50% sol.).....		
40.0g ammonium molybdate.....	94.0	9 500
0.4g vanadium pentoxide.....		
10.0g molybdenum phosphate.....	94.0	9 030
1.0 ml manganese nitrate (50%).....	99.5	7 790
10.0g molybdenum phosphate.....	94.0	10 400
3.0 ml manganese nitrate (50%).....	99.5	9 500
1.0g molybdenum metal powder.....	94.0	12 200
11.0g ammonium molybdate.....		
1.0 ml manganese nitrate (50%).....		
1.0 ml hydrogen peroxide (30%).....	94.0	12 290
10.0g tungstic acid.....		
30.0 ml ammonium hydroxide.....		
0.5g ferrous ammonium sulfate.....		
0.2g manganese tungstate.....	94.0	13 750
10g tungstic acid.....		
25.0 ml ammonium hydroxide.....		
0.5g manganese tungstate.....	94.0	6 320
10g tungstic acid.....		
25.0 ml ammonium hydroxide.....		
0.5g ferrous ammonium sulfate.....		

with the alumina content of the test pieces and the tensile-test data. The solution of ammonium molybdate and manganese nitrate allowed the least migration into unpainted areas and produced seals with the highest average tensile strength. Tentarelli et al. also observed that:

1. Concentrated metallizing solutions did not produce joints with higher seal strengths, resulted in more loose metallic particles on the ceramic surface after sintering than with a dilute solution, and displayed more migration.

2. Applying the metallizing solution to heated ceramic surfaces appeared to promote uniform coating.

3. The addition of thickening agents to the solutions did not improve the uniformity of the coatings or the seal strengths.

4. The seal strengths obtained by solution-metallizing were comparable to those obtained with low-temperature metallizing mixtures of metal oxides.

Solutions of molten-metal salts have also been used to metallize ceramic surfaces for subsequent joining operations. Straumanis and Schlechten of the University of Missouri School of Mines and Metallurgy, in investigating this process as a means to coat metals with titanium, did some work on coating ceramic surfaces (ref. 67). In this process, a mixture of 90-percent potassium or sodium chloride and 10-percent titanium powder is prepared and heated in a closed vessel under a helium shield until the mixture is molten; titanium powder usually contains 2 to 5 percent oxygen in the form of titanium oxide. After the mixture of metal salts is molten, the metal to be coated is lowered into the bath. The mechanism of coating is not clearly defined and several theories have been advanced to explain it. One states that the titanium oxide and potassium (or sodium) chloride react to form titanium chloride and potassium or sodium oxide; then, the titanium chloride and the metal to be coated react to form a metal chloride and titanium. The titanium is deposited as a film on the metal. Siebert et al. suggested that a reduction mechanism is responsible for depositing titanium on the metal (ref. 68). Of course, other reactions occur during the metallizing of a ceramic surface. The thickness of the coating highly depends on time

and temperature. At 950° C (1742° F), a titanium-rich layer, 0.0002 inch thick, was formed on a steel surface in 2 hours; the layer increased to 0.0004 inch in 6 hours. At 1000° C (1832° F), the layer thicknesses were 0.0004 inch after 2 hours and 0.0007 inch after 6 hours. Quinn and Karlak have simplified the procedures greatly and developed methods to coat ceramic surfaces with zirconium, hafnium, and uranium as well as titanium at temperatures as low as 600° C (1132° F) (ref. 69). To coat a ceramic surface, a thin titanium sheet is coated with a mixture of alkali or earth alkaline halides to a thickness of about 0.030 inch. The ceramic body is placed on the coated titanium sheet and the assembly is heated in an air furnace. The mixture of metal salts melts and flows over the titanium surface, protecting it from oxidation and depositing titanium on the ceramic surface. The thickness of the coating can be varied by regulating the time and temperature of heating.

Vapor-Deposited Coatings

Vapor-deposition processes used to deposit metal coatings on ceramic surfaces can be grouped in two major classifications: chemical vapor deposition and physical vapor deposition. Chemical vapor deposition may be defined as the deposition of elements or compounds in massive form or as a coating process by chemical reaction of the vapors of suitable compounds, usually at a heated surface. Intentional chemical reaction is not involved in physical vapor deposition; the material composing the coating is identical with the source material.

Several variations of the physical vapor deposition process have been used including:

1. *Sublimation and evaporation*.—The coating material is heated until the number of atoms and molecules leaving its surface is sufficient to produce the desired deposit on a ceramic substrate located some distance away. This process is often called "vacuum metallizing," although some nonmetals can also be deposited in this manner.

2. *Sputtering*.—Normal physical sputtering is characterized by the inert-gas ion bombardment of a cathode target, resulting in the ejection of atoms from the target surface into the

surrounding gas atmosphere. Deposition of these target atoms on a nearby substrate produces a thin coating of the target material.

3. *Ion plating*.—Thermally evaporated metallic atoms are ionized and accelerated in an electrical field. The ions impinge on the substrate surface with somewhat higher kinetic energies than in sputtering and with much higher energies than in sublimation or evaporation.

Reed and McRae coated all grades of alumina (up to 99.75-percent alumina) and 96-percent beryllia with molybdenum (ref. 70). The molybdenum was evaporated by a heated filament, and vacuum-tight coatings up to 0.0004 inch thick were deposited in less than 2 minutes. The ceramics were cleaned with water-detergent solutions and air-fired at 1000° C (1832° F). Before evaporation, the ceramic surfaces were further cleaned by a glow discharge. Joints prepared with the molybdenum-coated ceramics had tensile strengths of 20 000 psi for alumina ceramics and 15 000 psi for beryllia ceramics. Holmwood and Glang also used evaporation techniques to coat oxidized silicon wafers with a thin film of molybdenum (ref. 71). The source of the molybdenum vapor was a molybdenum rod heated by an electron beam in a vacuum (2×10^{-7} torr).

Various types of alumina have been metallized with a "particle bombardment" process, developed by Heil and his associates (ref. 72), where ions are sputtered from the target material and accelerated toward the substrate surface by high-frequency energy generated by a magnetron-type discharge. The surfaces of standard ASTM tensile test pieces made from a silica-free alumina ceramic (99.8-percent alumina) were metallized with niobium or vanadium by particle bombardment. The test pieces were joined together in pairs to produce specimens for evaluation. The tensile strength of seals made with niobium-coated ceramic surfaces ranged from about 6600 to 11 000 psi; the strength of seals made with vanadium-coated specimens was about 4500 psi. Alumina test pieces (99.5-percent alumina) were also metallized with tungsten or tantalum. The tantalum-metallized test pieces were copper-coated and brazed in pairs with the silver-copper eutectic

filler metal; the tensile strength of these joints ranged from 12 000 to 13 500 psi. The tungsten-metallized test pieces were nickel-plated and brazed with copper; the tensile strength of these joints was 9000 psi.

The high energy imparted to the ions during particle bombardment causes the particles to bond firmly to the target ceramic substrate; the substrate need not be heated to very high temperatures to ensure good bonding.

Sputtering techniques have also been used by Seeman to metallize alumina surfaces (ref. 73). A primer film of chromium was first deposited on the ceramic surface, followed by an intermediate layer of chromium plus copper, and a final layer of pure copper.

Before using the ion-plating technique to metallize ceramic surfaces (ref. 74), Mattox used it to deposit thin metallic films on metals and noted that this process had the following advantages over other vapor-deposition methods:

1. Since an inert gas is used to establish the glow discharge, the ceramic substrate surface is cleaned by ion bombardment before the film material begins to evaporate. However, after deposition begins, ion bombardment will sputter the deposited film, so that the deposition rate must always exceed the sputtering rate.

2. Ion plating tends to produce more adherent films than other methods.

3. The kinetic energy from ion bombardment is dissipated at the substrate surface as heat and enhances diffusion and reaction rates.

Mattox deposited multi-layer films on lead-zirconate-titanate substrates by ion plating. Aluminum was first deposited on the ceramic surface, because it reacts with the oxygen there and adheres well. To prepare the surface for soldering as well as brazing, a layer of copper or gold was deposited over the aluminum before the aluminum deposition was completed; thus, there was a bottom layer of aluminum and copper (or gold), and a top layer of copper (or gold).

Metal-Glass Powder Coating

Ceramic insulating materials used in the electronics industry have been metallized for many years with metal-glass powder mixtures. Finely

divided metal powders and glass frits are mixed with a suitable inorganic binder to form a paint that is applied to the area of the ceramic to be metallized, and the coated ceramic is fired to promote adhesion of the glass to both the ceramic and metal powder. The thin conductive coatings produced in this manner can be electroplated, or soldered connections can be made directly to them. Noble metals such as gold, palladium, and platinum have been used to metallize ceramics but silver is most common.

In a series of three articles (refs. 75 to 77) on producing thin conductive films on ceramic bodies, Lindquist discusses materials (metal powders, glass fluxes, and binders), coating techniques, and drying and firing methods. Sedenka conducted studies to determine the effect of firing temperature on the adherence of silver to ceramics (ref. 78). He found that adhesion depends on the chemical composition of the glass flux in the silver paint mixture and in the ceramic.

Ceramics have also been metallized by the thermal reduction of aqueous salt solutions of precious metals. The solutions used to deposit thin films of silver, gold, or other metals have been reviewed by Heritage and Balmer (ref. 79).

Electroplating

To ensure the production of reliable ceramic-to-metal seals, most metallized surfaces are coated with nickel, copper, or other metals. The metals are usually deposited by electroplating; however, in some cases, the coatings are produced by reducing oxides of the desired metal. These coatings perform several functions, depending on the method used to produce ceramic-to-metal seal. If the joints are to be brazed with conventional silver- or copper-base filler metals, the coatings serve the following purposes:

1. A metallizing layer is composed of metals and residual oxides not completely reduced during sintering. Such a surface is not conducive to good wetting by the brazing filler metal. Plating with nickel and/or copper eliminates the adverse effects of the surface on the wetting and flow characteristics of the filler metal.

2. When the metals used for metallizing are

not wet readily by low-temperature filler metals, plating provides the surface with a metal easily wet by such brazing alloys.

3. To a degree, the plated metal acts as a barrier to the penetration of the metallizing layer by the filler metal. Some filler metals react with the metals used for metallizing, and if the reaction is allowed to proceed too long, the filler metal may penetrate the metallized coating and lift it away from the ceramic. Metallized coatings are usually plated with nickel to retard penetration and copper to provide good wetting.

If the ceramic-to-metal joint is produced by methods other than brazing, the plating may serve other functions. For example, diffusion-welded joints require interface materials that promote diffusion between the metal and the metallized ceramic surface.

Typical electroplating bath compositions and procedures will not be reviewed here, because detailed information is available in standard references on this subject, as well as in the technical literature on ceramic-to-metal joints.

The metals used in ceramic-to-metal joints are frequently plated also. Depending on the metal, plating provides a surface easily wet by the filler metal, protection against oxidation of the metal surface during the brazing cycle, protection against intergranular penetration by the filler metal, and sustained cleanliness of the metal surface during storage.

JOINING PROCESSES

The choice of a joining process to fabricate ceramic-to-metal seals on joints is limited by the physical and mechanical properties of the ceramic materials. The first ceramic-to-metal joints were assembled by mechanical means, and while such techniques are still in use, the high-quality, vacuum-tight joints required by the electronics, nuclear, and aerospace industries are produced by the processes used to join metals. Metal-joining techniques can be divided into three major categories briefly discussed below.

Fusion Joining

The base materials are heated until they melt and fuse. The heat required for fusion is pro-

duced by an electric arc, an electron or photon beam, or the resistance of the base materials to an electric current. This category includes the numerous arc-welding and resistance-welding processes. There is little application of fusion joining in producing ceramic-to-metal seals, since ceramic materials cannot withstand the thermal shock associated with welding without cracking. The electron-beam welding of ceramic-to-metal joints has been investigated with limited success.

Solid-Phase Joining

All processes in this category accomplish bonding without changing the solid state of the joint's materials. While most of the processes require heat, the materials in the joint do not become molten. Pressure is usually required to produce joining. Several of the solid-state joining processes have been used to produce ceramic-to-metal seals. Among them are the following: diffusion welding (or bonding), pressure welding, gas pressure bonding, and ultrasonic welding. Electroforming or electrodeposition welding and high-energy welding are also included.

Liquid-Solid Phase Joining

This category includes soldering and brazing—the processes most widely used in fabricating ceramic-to-metal seals. The joint assembly is heated to a temperature below the melting temperature of the base materials but above the melting temperature of the filler metal; thus, a liquid phase is formed at the interface between two solid members, and the molten filler metal is distributed throughout the joint by capillary attraction. Joining is accomplished when the filler metal solidifies.

Adhesive bonding procedures are used to join ceramics to metals for some applications, but not to produce ceramic-to-metal seals, since adhesives have a limited service temperature range (350° F or below for continuous service) and are not suitable for vacuum-tight assemblies. Ceramic adhesives developed for joining metallic materials may be useful in joining ceramic to metals if the joints are not stressed.

JOINT EVALUATION

The soundness of ceramic-to-metal joints and seals must be assured to guarantee the performance of the structure in which they are incorporated. Thus, strict quality control of all phases of the manufacturing process is required from the inspection and testing of all incoming materials to the final inspection and evaluation of the finished product. Tests to determine the properties of ceramic-to-metal joints are an essential part of any quality control program. Such tests fall into the following categories: mechanical tests, electrical tests, leak tests, thermal tests, and tests associated with the service requirements for the joints. These test data should be supplemented by information gathered from visual and metallographic examination of failed joints, so that the processing techniques can be changed to correct apparent deficiencies.

Ideally, it should be possible to determine the properties of a particular ceramic-to-metal joint and extrapolate data for the design of other joints. This is difficult to do because of the current inadequacies of the test procedures and the lack of reproducibility caused by variations in the compositions and properties of the ceramic materials. However, it is possible to evaluate the performance of a ceramic-to-metal joint and establish quality control measures to ensure compliance with the service requirements. Extensive efforts to advance the state-of-the-art in testing ceramics and ceramic-to-metal joints have been initiated by Government, industry, and the technical societies. Shook conducted a survey of the methods used to determine the mechanical properties of brittle materials including ceramics; each test was analyzed to discover its capabilities and limitations (ref. 80). The American Ceramic Manufacturers Association, in an attempt to establish standards for many properties of high-alumina ceramics (ref. 81), has listed about 20 physical, mechanical, and electrical properties of ceramics along with references to test methods and testing conditions. Properties are specified for alumina ceramics on the basis of their alumina content: 80 to 90, 90 to 96, and over 96-percent alumina. Many of the methods used to determine the properties of ceramics and ceramic-to-metal

joints are contained in specifications issued by the American Society for Testing and Materials and various Government agencies.

The tests used to evaluate the properties of ceramic-to-metal joints are similar to those used to acquire property data on ceramics and metals. Many tests were derived from those in use by metal fabricators. There are many variations of each test, and despite efforts to standardize there is little industry-wide agreement on the exact testing method, test specimen, or interpretation of results. As a consequence, it is difficult or impossible to correlate data from different manufacturing facilities.

This report will not discuss test procedures in detail, but will indicate the tests used and reference them for further study. Clarke, Ritz, and Girard have prepared an excellent review and discussion of these tests (ref. 28).

Mechanical Tests

Tensile Strength

Tensile strength tests measure the strength of a ceramic-to-metal joint when opposing forces are applied perpendicular to the joint interface and away from the joint. The ASTM tensile test is the nearest equivalent to a standard test that has been accepted and used by industry (ref. 82). The test specimen is prepared by metallizing and brazing together two halves of a ceramic body having a specified size and shape (fig. 6). After being mounted in a standard tensile machine, the specimen is tested in tension to failure. Aligning the specimen so that only pure tension loads are applied has been difficult, and shoulder breaks in the ceramic test pieces are common. These results are frequently interpreted as a positive indication that the joint strength exceeds that of the ceramic, while failure may be caused by improper alignment or stress concentrations induced by the mounting fixtures. While this test is used widely by industry, the cost of the test pieces is relatively high because they must be specially made by a ceramic manufacturer; consequently, it is rare that the number of tests required for a statistical analysis is conducted.

Other tests have been used to measure the tensile properties of ceramic-to-metal joints. Luks and Magee proposed the use of two ceramic hemispheres metallized and brazed together to form a hollow sphere; fluid pressure is then applied until joint failure occurs (ref. 83). Schuck devised a test specimen that was prepared by brazing a metallized ceramic disk inside a Kovar sleeve (ref. 84). Rubber disks were placed inside the Kovar sleeve on either side of the ceramic disk; pressure was applied to the rubber disks by means of steel plugs. The entire assembly was placed in a dynamometer and the pressure was increased in 200-pound increments until a leak developed. As the pressure was increased, the rubber disks were compressed and bulged outward, exerting a radial force on the Kovar sleeve. The pressure at failure was defined as the seal or joint strength. This test is somewhat similar to a peel test.

Peel Strength

Various types of peel tests have been developed to measure the force required to pull a thin metal strip from the ceramic substrate to which it has been brazed. These tests are commonly used by industry, since the specimen is easy to make and test. Equipment for the test is readily available or it can be constructed. To make the test specimen, a thin strip of the metal to which the ceramic will be bonded in the final assembly is brazed to a metallized ceramic; a small tab is left unbrazed so it can be attached to a fixture on the peel test equipment. Using equipment as shown in figure 7, the strip of metal is peeled from the ceramic (ref. 53). A record of the force required for peeling is produced on a strip chart recorder. Sometimes the test is conducted without force measurements and attempts to correlate bond strength with the visual appearance of the joint members may yield inaccurate results.

Flexure Strength

This test measures the strength of a ceramic-to-metal joint when a bending moment is applied. The joint members consist of two round or flat ceramic sections whose length-to-cross-

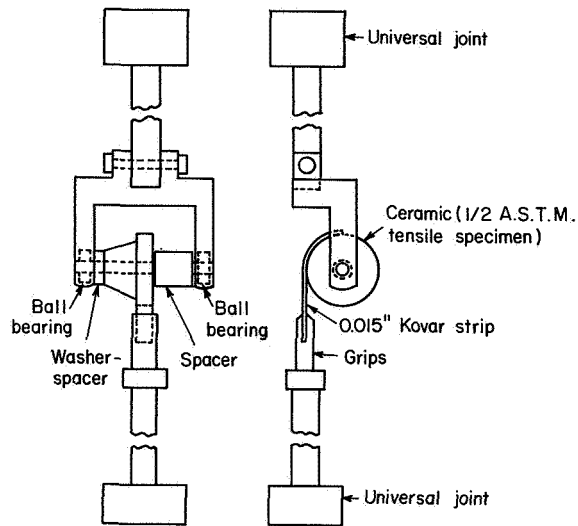


FIGURE 7.—Schematic of drum peel test apparatus (ref. 53)

section ratio is large. The ends of the sections are metallized and then butt-brazed to a relatively thin sheet of metal. The test can be conducted with three- or four-point loading. In the first case, equal forces are applied in a direction parallel to the joint interface at points equidistant from the joint; a third force is applied in an opposing direction at the center of the specimen. In four-point loading, two equal forces are applied in a direction parallel to the joint interface at points equidistant from the center of the specimen; two equal opposing forces are also applied at points equidistant from the center of the specimen but not directly opposite the points where the original forces were applied. Figure 8 shows four-point loading in the specimen used by Pincus to determine flexure strength (ref. 85).

Shear Strength

This test measures the resistance of the ceramic-to-metal joint to opposing shearing forces. Because of the difficulty in aligning the specimens and obtaining pure shear stresses, this test is not used widely. Reed et al. used the specimen shown in figure 9 to measure the shear strength of a ceramic-to-metal joint (ref. 86). After metallizing the inside diameter (I.D.) of

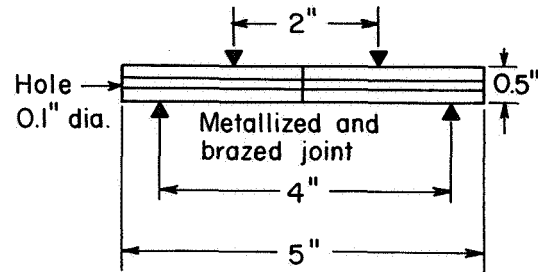


FIGURE 8.—Bending strength test specimen

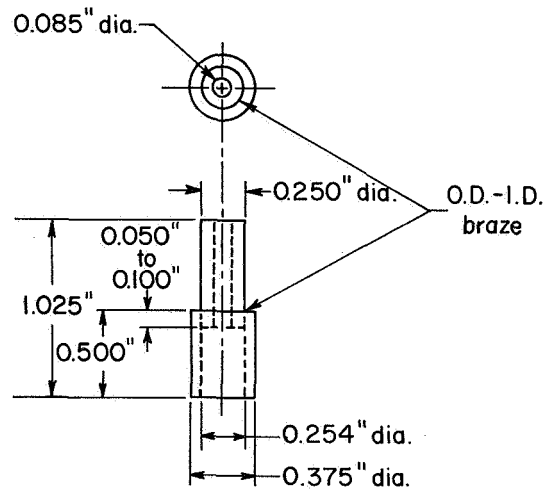


FIGURE 9.—Shear strength test specimen (ref. 86)

the large tube and the outside diameter (O.D.) of the small tube, the tubes were brazed together. Reed and his associates claimed the following advantages for this specimen: the joint could be shear-loaded in a conventional compression tester, the specimen could be leak-tested, and residual stresses could be induced in the joint by properly selecting and locating the joint members.

Electrical Tests

Since ceramic-to-metal seals are used for electronic applications, volume resistivity, breakdown voltage, and electrical losses must be measured to determine the effects of the metallizing and joining operations. An accurate de-

termination of electrical losses is particularly important for ceramics used as windows in high-frequency devices for the passage of microwave energy. In studying the factors that contribute to radio-frequency power losses in ceramic-to-metal seals, Reed et al. distinguished between conductive losses and dielectric losses and devised techniques to measure these quantities and determine how they are affected by the metallizing materials, the metallizing process, and the plating materials (ref. 86). Conductive and dielectric losses were determined at low and high radio-frequency power levels. The direct-current resistivity of metallizing was also measured as a function of temperature.

Leak Tests

Leak tests are required when the ceramic-to-metal joint is used as a seal in high-vacuum devices. The helium mass spectrometer leak detector is most commonly used to detect the presence of small leaks. The joint to be evaluated is sealed to the mass spectrometer tube and the area around the joint is flooded with helium. The flow rate of helium through a leak will be detected and measured by the mass spectrometer. The test is extremely sensitive. Considerable experience is required to pinpoint very small leaks. Complete details on the use of this equipment can be found in references on vacuum techniques.

Leaks of larger size can often be detected visually with bubble tests or dye tests.

Thermal Tests

Thermal Conductivity

Thermal conductivity tests measure the quantity of heat that flows across a ceramic-to-metal joint of known dimensions in a specified length of time when a temperature differential across the joint exists. This characteristic has an important bearing on the heat dissipation properties of the structure in which the ceramic-to-metal seal is used. The measurement of heat conductivity is described in ASTM Specification C408-58 (ref. 87).

Thermal Shock and Thermal Cycling Tests

Data on the resistance of the ceramic-to-metal joint to thermal shock and to repeated heating and cooling cycles may be required by the service conditions under which the joint will function. The test variables (maximum and minimum temperature, heating and cooling rates, number of cycles, time between cycles, and test environment, etc.) must be specified in the joint requirements.

The thermal shock resistance is determined by heating the joint to a specified temperature; after equilibrium is established, the joint is cooled rapidly and as uniformly as possible by immersing it in a liquid maintained at a specified temperature. Joints are leak-tested after each thermal-shock cycle.

Thermal cycling tests are performed to determine the behavior of the ceramic-to-metal joint when it is subjected to repeated heating and cooling cycles, such as those required by intermittent operation of a device. The joint is heated until a predetermined temperature is attained. After a specified interval, the joint is cooled to the starting temperature and the cycle is repeated as often as necessary. The heating and cooling rates are usually specified also. Again, leak tests are performed to determine the effect of thermal cycling on the soundness of the ceramic-to-metal joint.

Other Tests

In addition to the tests discussed above, other tests may be required to determine the behavior of the ceramic-to-metal joint under special circumstances. Thus, it may be necessary to measure or determine the resistance of the joints to vibration and shock, to corrosive liquids and vapors, to damage by radiation, and to oxidation at high temperatures.

In addition to standardized tests for determining the properties of ceramic-to-metal seals, there is a pressing need for good nondestructive testing methods to evaluate the overall quality of seals. Ultrasonic and X-ray procedures have been used to some extent, but neither method offers the reliability and versatility required by industry.

CHAPTER 4

Theory of Ceramic-to-Metal Joining

Although ceramic-to-metal joints have been made successfully for many years, a completely acceptable theory of bonding has not yet been developed. Much of our knowledge concerning the formation of ceramic-to-metal joints is based on observations rather than on a basic understanding of the reactions that occur during joining. As a result, ceramic-to-metal joining has developed mainly on an empirical rather than a scientific basis. The same situation prevailed in metals joining; however, progress in this area has been more pronounced because extensive research on the fundamental nature of joining has been conducted in response to the critical requirements of industry and Government.

The lack of understanding regarding bonding is a direct consequence of the number of variables associated with the joining process. The structure of ceramics generally is more complex than that of most structural metals, and, until recently, the importance of knowing the complete history of the fabrication of ceramics from the raw materials stage to the finished product was not realized. The development of the single-phase metal-oxide ceramic for critical assemblies has alleviated this situation somewhat. Added to the uncertainties regarding the base materials used in ceramic-to-metal joints are the variables associated with the preparation of the ceramic for joining and the joining operations themselves.

Many factors contribute to bond formation in a ceramic-to-metal seal or joint, among which are the following: chemical interactions between the joint materials, diffusion across the metal-ceramic interface, mechanical interlock-

ing of one phase with another because of microscopic surface roughness, and the penetration of glassy phases into metallic phases. The extent to which these mechanisms predominate depends on the selected joining technique, the characteristics of the individual joint materials, and on the process variables.

Since Pulfrich and Vatter first produced reliable ceramic-to-metal joints, numerous investigators have studied the mechanisms of bonding and have advanced theories to explain their observations. The theories that have received the most emphasis include the alumina reaction theory, the molybdenum oxide theory, the glass migration theory, and the metal ion-metal theory.

In his early patents on ceramic-to-metal sealing, Pulfrich set forth several recommendations for obtaining sound joints (refs. 1 to 4). He metallized the ceramic surface by coating it with a suspension of finely divided molybdenum particles and then firing the coating in a controlled atmosphere within a closely limited temperature range. Once metallized, the ceramic was electroplated and brazed to the metal with a silver-base filler metal. Pulfrich emphasized that glassy phases should be avoided at the joint interface and further specified that:

1. The metal for metallizing should have a melting temperature about 200°C (392°F) higher than the metallizing temperature, since a porous sintered surface promoted adherence of the filler metal to the metallizing metal.

2. The ceramic should have a eutectic bond that melts about 300°C (572°F) below the softening temperature of the ceramic body and

about 200° C (392° F) below the metallizing temperature.

3. The metal to which the ceramic is ultimately joined should have a melting temperature well above the metallizing temperature and should match the expansion coefficient of the ceramic as closely as possible.

4. The filler metal should melt below the melting point of the ceramic's lowest melting eutectic. Neither the filler metal nor any alloy formed between the filler metal and the base metal should react with the metallizing metal.

Pulfrich speculated that the molybdenum particles were wet by the liquid formed by the eutectic constituent of the ceramic. He noted that the furnace atmosphere should contain enough hydrogen to maintain most of the molybdenum as a metal; however, enough oxygen (about 0.25 percent) should be present to form a trace of molybdenum oxide which subsequently melts and improves bonding. During cooling the eutectic liquid should recrystallize completely to form a crystal structure free from residual glass. Thus, the molybdenum particles would be locked within the crystal rather than within a glass flux.

Although Pulfrich did not advance a formal theory, he was aware of the role of chemical reactions and liquid phases.

ALUMINA REACTION THEORY

In 1953, Pincus attempted to explain the reactions during the molybdenum-manganese method of metallizing (ref. 88). Assuming that manganese is oxidized to manganous oxide in any hydrogen atmosphere whose dewpoint is more than -65° C (-85° F), he traced the chain of events that takes place during sintering. At 1000° C (1832° F), a solid-phase reaction between alumina and manganous oxide forms manganese aluminate spinel at the interface, although no bonding occurs; at 1200° C (2192° F), this compound enters a liquid phase. At 1400° C (2552° F), appreciable sintering of the molybdenum particles occurs, and the liquid spinel locks the hardened layer to the ceramic. Upon cooling the liquid phase forms a glass that appears to extend into the metal layer; the alumina surface appears to be corroded. These

observations were verified by microscopically examining tapered sections of metallized ceramics; the tapered section elongated the ceramic-metal interface for easier study.

Pincus extended his theory to cover the metallizing of forsterite ($2 \text{ MgO} \cdot \text{SiO}_2$), where a reaction at the ceramic-metal interface forms a manganese-containing liquid that again locks the sintered molybdenum particles to the ceramic.

According to this theory the strength of seals made to a 100-percent alumina body should be as strong, or stronger, than seals made to a 90-percent alumina body; experimentally, this is not the case, because the difficulty in making seals increases with increasing alumina content. Workers at Sperry Rand have indicated that other additives, particularly silica, to the metallizing mixture are more effective in promoting bonding than manganese (ref. 53).

MOLYBDENUM-OXIDE THEORY

In a later paper, Pincus suggested that bonds between pure molybdenum and high-alumina ceramics were chemical in nature and depended on a reaction between molybdenum oxide and aluminum oxide (ref. 85). He conducted metallizing studies in a hydrogen atmosphere whose dewpoint was varied between +5° and -68° C (+40° and -90° F.); joints were examined microscopically to verify the reactions during metallization. The theory depends on the controlled oxidation of the molybdenum particles and an interface reaction between the metal oxide and the ceramic. Even if molybdenum oxide is formed by heating molybdenum in air or a wet hydrogen atmosphere, it volatilizes at 600° to 700° C (1112° to 1292° F), well below normal sintering temperatures. The validity of this theory was not confirmed by later work conducted at Sperry Rand (ref. 53).

GLASS MIGRATION THEORY

The glass migration theory, well substantiated by experimental data, proposes that the strength of ceramic-to-metal joints made by conventional means depends on the glass-phase content of the ceramics. This theory, attributed to Cole and Sommer, is the result of continuing

work initiated by Cole and Hynes (refs. 89 and 33). Metallizing studies were conducted using molybdenum-manganese, molybdenum-titanium, and pure molybdenum materials and 94- and 99-percent alumina ceramics. The results of these studies at various sintering temperatures are summarized in table 10. The seal strengths obtained with 94-percent alumina ceramic were greater and more consistent than those obtained with the 99-percent alumina ceramic. Photomicrographs showed that the glassy phase of the 94-percent ceramic had migrated into the metallizing coating and surrounded the molybdenum particles. Cole and Sommer suggested that manganese and titanium oxidized during the heating process and reacted with the ceramic to reduce the viscosity of the glassy phase; then, the glass was free to migrate slightly and lock the ceramic to the molybdenum coating. However, the presence of these metals did not appear to be essential, since excellent seal strengths were obtained with pure molybdenum alone.

TABLE 10.—*Results of Tensile Tests of Ceramic-to-Metal Seals*

[From ref. 89]

Alumina, percent	Metallizing sintering temperature, °C	Tensile strength of seals (lb/sq. in.)		
		80 per- cent Mo 20 per- cent Mn	97 per- cent Mo 3 per- cent Ti	100 per- cent Mo
99-----	1700	2900	6600	1700
	1600	750	2700	600
	1500	3100	2900	220
94-----	1700	9400	12 000	9600
	1600	9700	*12 000	13000
	1500	8000	10 100	10600

*Average values based on several hundred production control tests.

Since virtually no glass is present in the 99-percent alumina ceramic, the adherence in these ceramic-to-metal seals must be explained by another mechanism. Cole and Sommer suggested that the metallizing components reacted to form a compound that wet both the alumina surface

and the molybdenum particles; this explanation is supported by the evidence that stronger seals were obtained with a metallizing mixture containing molybdenum and titanium than with molybdenum alone. The possibility that bonding resulted from an ion exchange was not discounted, however.

In conjunction with this theory, the addition of glass or glass-forming materials to metallizing mixtures has been investigated; such additives have proved useful in promoting bonding.

OTHER THEORIES AND MECHANISMS OF ADHERENCE

Several other theories and suggested mechanisms of adherence have been advanced to explain the phenomenon of ceramic-to-metal bonds.

Helgesson used the electron probe to examine the microstructure produced when high-alumina ceramics (94.0-, 99.0-, and 99.9-percent alumina) were metallized with a standard molybdenum-manganese metallizing mixture (ref. 90). In contrast to other investigators, Helgesson reported greater seal strengths with higher alumina ceramics. He concluded that bonding was caused by chemical forces.

Floyd investigated the metallizing of high-alumina ceramics containing various amounts of a $\text{MgO-SiO}_2\text{-CaO}$ glassy phase; the metallizing materials were pure molybdenum, pure manganese, and an 80-percent molybdenum 20-percent manganese mixture. Floyd noted that bond strength increased with higher contents of the glassy phase and with the formation of the manganese aluminate spinel. His work appears to support the alumina reaction and glass migration theories (ref. 34).

Reed and Huggins metallized high-alumina ceramics with various mixtures and, on the basis of electron microprobe analyses, reported that molybdenum did not dissolve or diffuse in the reacted metal-oxide phases or the alumina-crystal phase of the ceramic, and the metal oxide compounds of the metallizing layer reacted with the alumina-crystal phase and diffused into the ceramics (ref. 91).

Cowan et al. recently developed procedures using tungsten powder plus small concentra-

tions of yttria to metallize silica-free, high-alumina ceramics for service in a cesium environment (ref. 92). They suggested that WO_3 forms at low temperatures and reacts with yttria in the grain boundaries of the ceramic to form yttrium tungstate. At higher temperatures, the yttrium tungstate is reduced and yttrium migrates into the tungsten metallizing layer to lock the particles in place. Kiwak has discussed several modifications of this metallizing procedure and recommends the use of a $\text{Mo-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixture to obtain sound bonds (ref. 93).

In research directed toward the development of low-temperature sealing techniques, Tentarelli et al. advanced the insulator-semiconductor-metal theory to explain bonding. They suggested that a molybdenum nonstoichiometric oxide semiconductor is formed at the ceramic-to-metal interface and that electronic bonding is responsible for adherence (ref. 64).

WETTING AND CERAMIC-METAL INTERFACE REACTIONS

Studies investigating the fundamental nature of wetting phenomena and the reactions that occur along the ceramic-to-metal interface are very similar to studies investigating the wetting of a base metal by a brazing filler metal. Van Vlack, in an excellent discussion of the ceramic-metal interface, states that bonding between ceramic and metallic phases depends on interphase reactions and the atomic structure across the interface (ref. 94). He indicated that the strongest boundaries require primary ionic and

covalent bonds and low interfacial energies. Epitaxial coherence between crystalline ceramics and metals is necessary if a glassy phase is absent. Greater adherence between ceramics and metals occurs when there is a large interfacial area.

When a drop of liquid is placed on a flat surface, it may spread or remain in an essentially spherical form. The thermodynamic driving force for spreading or wetting is a decrease in the free energy of the system. Extensive studies have been conducted by Kingery and his associates to develop procedures to measure surface energies, interfacial energies, and contact angles at metal-ceramic interfaces, and to examine metal-ceramic reactions and the effect of certain elements on the formation of bonds (refs. 95 to 99).

Additional research on glass-metal systems by other investigators has resulted in bonding theories (ref. 100) that may be applicable to ceramic-metal systems as well. In working with the adhesion of porcelain enamels (glass) to metals, King et al. set forth the following statements regarding adherence (ref. 101):

1. The enamel at the interface must be saturated with a metal oxide that, in solution with the enamel, is not reduced by the metal.
2. Adherence appears to result from metal-to-metal bonding between the atoms in the base metal and metallic ions in the enamel.

Thus, adherence appears to be chemical in nature. A thorough review and critique of the theories and mechanisms of bonding has been prepared by Clarke et al. (ref. 28).

Ceramic-to-Metal Joining

FUSION JOINING

Electron-Beam Welding

In investigating the direct fusion joining of ceramic materials to themselves and to metals, electron-beam welding is the most promising of the available fusion welding processes, because the electron beam can be precisely controlled to produce an extremely small spot weld or weld bead with minimum melting of the joint materials. Also, reactions between the joint materials and the atmosphere are minimized or eliminated by the high-vacuum nature of this process.

Hokanson, Rogers, and Kern of the Hamilton Standard Division of the United Aircraft Corporation were among the first to evaluate the potentialities of this joining method (ref. 102). Because of the high accelerating voltage, the spot diameter of the Hamilton-Zeiss high-power-density electron-beam unit could be controlled to a diameter less than 0.010 inch. An optical viewing system was provided for precise observation of the welding process. With this equipment, butt- and edge-welds were made with ceramic bodies having alumina contents of 85, 96, and 99.75 percent. Preheating and controlled cooling rates, particularly above 1200° F (649° C), were required to eliminate cracking. The most suitable welds between ceramics were made with a high-voltage, low-current electron beam at about 30 ipm; slower welding speeds produced a weak glassy structure. Flexure tests indicated that a butt-welded joint was about 20 percent as strong as the ceramic. Molybdenum-to-ceramic pin joints were welded as well as crack-free joints between a 96-percent

alumina body and the following metals: molybdenum, tungsten, niobium, and Kovar. While welding these joints, the electron beam was positioned slightly off the joint centerline over the metal; thus, the metal melted and flowed over the ceramic. This welding technique is common in the case of metals with widely differing melting temperatures.

Electron-beam welding was investigated as a method to fabricate ceramic-to-metal seals for use in a thermionic energy conversion system. Engineers at the Los Alamos Scientific Laboratory reported only limited success in welding a ceramic body to molybdenum and a molybdenum-titanium alloy metallized with nickel (ref. 103). In a somewhat similar program conducted by the Bendix Corporation, Dring indicated that strong joints between molybdenum and an alumina ceramic were obtained by electron-beam welding; the ceramic surface was metallized by the moly-manganese process (ref. 104). Joining occurred only when intimate contact between the metal and ceramic was achieved. During welding, the beam was controlled to fuse the molybdenum sheet to the metallized layer. The joints were crack-free and exhibited excellent peel strength; joint failure occurred at the ceramic-to-metallizing interface.

Direct Fusion

Stablein and Araoz of the Argonne National Laboratory have used an arc-image furnace to produce direct fusion between ceramics and metals (ref. 105). In this type of furnace, heat is produced by reflecting and refocusing the light from a high-intensity (10 kilowatt)

carbon-arc lamp onto a small area, about $\frac{1}{2}$ inch in diameter, where the specimen is located. The large temperature gradient produced by focusing heats a small area on the specimen while the remainder remains relatively cool. The heat from the furnace can be controlled by an adjustable diaphragm that reduces the cone of light reaching the specimen; also, a screen acts as a filter to reduce the total light energy. The specimen is mounted in a rotating holder so that the specimen is heated uniformly. This equipment has been used to produce butt and tee joints in high-purity alumina tubing (99.75-percent alumina). The tubing was cut to size on a diamond saw without using flux or cement. There was no reduction in the internal diameter of the tubing.

Porembka reported that in directly fusing ceramics to metal at the Columbus Laboratories of the Battelle Memorial Institute (ref. 106), zirconium oxide was joined to tungsten by melting the oxide in contact with the metal in a vacuum. In this approach, the wetting of the solid surface by the molten phase was of primary importance. The absence of an intermediate layer at the joint interface suggested that joining occurred as the result of chemical bonding. However, a slight amount of roughness at the joint interface was noted and indicated that some mechanical locking may have occurred.

Buyers (Hughes Research Laboratories) produced joints between tantalum and a stabilized zirconia ceramic at about 2000° C (3632° F) (ref. 107). The ceramic and tantalum workpieces were placed in contact vertically, with the metal resting on the ceramic. Then, the assembly was heated rapidly to 1955° to 1995° C (3551° to 3623° F) by an induction coil. At this temperature, the interface between the ceramic and metal disappeared as the bond was formed. Intermediate compounds that formed spontaneously at this temperature were identified by X-ray diffraction powder patterns. For seals using zirconia stabilized by oxides, the following compounds were identified: tantalum zirconate, yttrium tantalate, tantalum silicide, aluminum tantalate, and magnesium tantalate. The exact mechanism of joining has not been established as yet.

SOLID-PHASE JOINING

Research in this area of joining has been concentrated on fabricating "graded powder" seals, i.e., a ceramic-metal composite material whose composition varies continuously from a ceramic to a metal. Knecht proposed this method, using the reasoning behind the production of graded seals between hard and soft glasses (ref. 108). In an experimental program at the Air Force Electronic Components Laboratory, the feasibility of the technique was demonstrated by producing a closed-end tube consisting of a metal cylinder with a ceramic body.

From 1954 to 1956, Dunegan developed procedures to produce a ceramic cylinder (0.8 inch O.D., 0.64 inch I.D., and 0.4 inch thick) that was metallized on both ends (ref. 109). In producing the cylinder, a mixture of selected metal powders and a mixture of ceramic and metal powders were used. A thick, smooth layer of metal powder was spread over the die area. Then, a thicker layer of the ceramic-metal powder mixture was spread over the metal powder. Finally, another thin layer of metal powder was spread over the ceramic-metal powder mixture. The die set was assembled and pressure was applied to produce a green powder compact. The compact was prefired at about 250° to 300° C (482° to 572° F) to remove the volatile constituents and then sintered at temperatures exceeding 1000° C (1832° F).

The most successful ceramic-to-metal system consisted of an 85-weight percent alumina and a 30-weight percent spinel ($\text{Fe}_{0.5}\text{Ni}_{0.5}$) ($\text{Al}_{1.0}\text{Cr}_{1.0}$)₂O₄ that was metallized with a tungsten-copper-nickel alloy plus 25-weight percent chromium. Dunegan stated that the success of the pressed powder seal depended on several factors:

1. The thermal expansion and contraction of the metal and ceramic must be very similar.
2. The firing temperature must be the same for both materials.
3. The firing shrinkage must be the same for both materials and occur at the same rate.
4. There must be a reaction between the ceramic and metal. Bonding appears to occur through an oxide phase.

Dring also investigated the fabrication of a

graded-powder seal for use in thermionic converter applications (ref. 104). Since a closed-end cylinder about 1 inch in diameter was typical of the envelopes used in many converters, this research was to produce an envelope in which a refractory metal formed the closed end and the cylinder wall material was graded from a metal to a pure ceramic at the open end. The most successful composite envelope was fabricated from 12 gradations of alumina and tungsten powders as shown in table 11. The 12 powder mixtures were loaded layer by layer into a die; pure alumina was added at each end of the compact to reduce problems with laminations in the high-tungsten area. The compacts were pressed at 30 000 psi. After removal from the die, the compacts were air-dried and machined to remove the excess alumina from each end. Then, the compacts were sintered at 3365° F (1852° C) for 8 hours. Several envelopes were produced, graded from 95 percent tungsten-5 percent alumina at the closed end to 100 percent alumina at the open end. It was not possible to use pure tungsten at the closed end

of the cylinder because of the laminations produced by the pressing operation. Although the envelopes were not completely vacuum-tight, the leak rate was very low.

The development of a graded-powder ceramic-to-metal seal for high-temperature service in a cesium environment was also undertaken by Bristow et al. (ref. 11). The metallic members of the seal had to be joined to a multilayered or graded structure whose composition varied from a predominantly oxide core to a predominantly metallic surface. The oxide core had to be electrically insulating. Graded-powder structures were produced by hot-pressing five-layer compacts whose composition varied from 75 percent molybdenum-25 percent alumina at the metal end to 5 percent molybdenum-95 percent alumina at the ceramic end. The powders were placed in an induction-heated die and sintered for 10 minutes at 1600° C (2912° F) under 4000 psi. The necessity to use an alumina-rich composition as the core layer increased the problems of fabricating a dense structure that was vacuum-tight and electrically insulating.

TABLE 11.—*Gradations of Powder Used in Tungsten-Alumina Structure*

[From ref. 104]

Gradation Number	Tungsten ^a weight	Alumina ^b weight	Phosphoric ^c acid solution, cm ³	Percent by weight		Percent by volume	
				Tungsten	Alumina	Tungsten	Alumina
0	0	3.0	0.21	0	100	0	100
1	13.30	0.70	0.10	95	5	80	20
2	8.80	1.2	0.10	88	12	59	41
3	3.08	0.92	0.10	77	23	40	60
4	2.56	1.44	0.10	64	36	26	74
5	1.50	1.50	0.10	50	50	16.5	83.5
6	1.08	1.92	0.13	36	64	10	90
7	0.93	2.07	0.14	31	69	8.15	91.85
8	0.52	1.48	0.10	26	74	6.5	93.5
9	0.40	1.60	0.11	20	80	4.7	95.3
10	0.26	1.74	0.12	13	87	2.86	97.14
11	0.12	1.88	0.13	6	94	1.24	98.76
12	0	21.0	1.45	0	100	0	100

^aTungsten—99.75% #3 tungsten powder (table 1) 0.025%—325 nickel powder

^bAlumina—73.5% B (Table II)

24.5% A (Table II)

2.0% magnesium stearate

^cPhosphoric acid solution—15% aqueous solution of H₃PO₄

Although the results of these studies were encouraging, the need for more research was indicated.

Porembka discussed the fabrication of a graded cermet bond between tungsten and thoria using a series of tungsten-base cermets with decreasing tungsten content and a series of thoria-base cermets with increasing thoria content (ref. 106). Cermets are made by mixing metal powders with the ceramic batch. Densification of the cermet and bonding to the parent materials can be accomplished by sintering or hot-pressing methods. Porembka stated that such a bonding method was particularly useful in joining materials with widely differing expansion coefficients.

GAS-PRESSURE BONDING

Porembka used gas-pressure bonding to fabricate joints between niobium and high-purity ceramic materials (ref. 110). Of the two metal-ceramic systems selected for study, the niobium-chromium-alumina system is a three-component system in which the intermediate material provides the necessary diffusion characteristics with niobium; its oxide is completely soluble in alumina. The niobium-zirconia system represents a two-component system in which the metal oxide has limited solubility in the ceramic. Two types of specimens were used for the study of the niobium-chromium-alumina systems as shown in figure 10; the stainless steel sections were incorporated in each specimen for attachment to the grips in a tensile testing machine. The cermet section was composed of 50-volume percent chromium and 50-volume percent alumina. The specimens were assembled in a capsule that was evacuated and sealed before bonding. Isostatic hot-pressing was conducted for 3 hours with the temperature 2200° to 2300° F (1205° to 1260° C) and pressure 10 000 psi.

Niobium-zirconia specimens were prepared in the same manner as the niobium-chromium-alumina specimens; no intermediate material was present in these joints. Isostatic hot-pressing was conducted under the conditions listed above.

Reduced-section tensile specimens were machined and tested. The test data are summarized

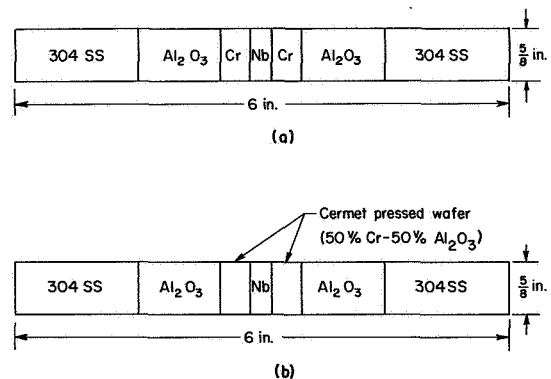


FIGURE 10.—Alumina-chromium-niobium specimen assemblies (ref. 110). (a) Metal wafer composite; (b) cermet composite

in table 12 for the niobium-chromium-alumina system. The specimens prepared with cermet intermediate materials fractured during machining, so that no tensile data were obtained. Similarly, all but one of the niobium-zirconia specimens fractured during machining; a tensile strength of 1370 psi was obtained from this single specimen.

Additional studies conducted during this program included metallographic examinations of niobium-chromium-alumina and niobium-zirconia joints, microprobe analysis of a niobium-chromium-alumina joint, and thermal cycling tests of niobium-chromium-alumina joints.

The following conclusions were advanced:

1. Gas pressure bonded joints between chromium and alumina showed higher strengths than those produced by other joining methods.
2. The infiltration of the metal phase into the asperities and surface pores of the ceramic was a major factor in the strength of pressure-bonded joints.
3. Diffusion in the chromium-alumina and chromium oxide-alumina systems was not measurable by microprobe analysis. No metallographic evidence of diffusion was noted.
4. Niobium-zirconia joints produced by gas-pressure bonding were weak. Joint failure occurred through an intermediate phase formed by diffusion between niobium and zirconium.
5. Niobium-chromium-alumina joints were resistant to limited thermal cycling to 2300° F (1260° C).

TABLE 12.—*Tensile Strength of Pressure-Bonded Niobium-Chromium- Al_2O_3 Assemblies*^a

[From ref. 110]

Specimen Number	Chromium oxidation treatment ^b	Gage diameter, inches	Breaking load, psi	Breaking stress, psi	Location of fracture
CNA-1-----	None-----	0.345	502	5550	Al_2O_3 ^c
CNA-2-----	None-----	.375	878	10 700	Cr-Nb interface
ANC-10-----	8 hr at 700° C-----	.405	856	6700	Al_2O_3
ANC-11-----	do-----	.465	846	6500	Al_2O_3 ^c
ANC-12-----	do-----	.410	936	7100	Al_2O_3 ^c
ANC-13-----	2 hr at 700° C-----	.441	916	6100	Cr-Nb interface
ANC-14-----	do-----	.476	931	5400	Al_2O_3 ^c
ANC-15-----	do-----	.441	882	5900	Al_2O_3 ^c

^a All specimens tested at room temperature at strain rate of 0.02 in./min.^b Oxidation conducted in 0.1 atm oxygen.^c Fractures in shoulder area of reduced section within Al_2O_3 components.

Diffusion Bonding

Only limited research has been conducted on diffusion bonding for fabricating ceramic-to-metal joints, although this process is used extensively in metals joining. In this method of joining, the carefully prepared workpiece surfaces are held in close contact by applying pressure, and joining occurs at temperatures below the melting temperatures of the base materials. An intermediate material may be used to promote or limit diffusion. Diffusion bonding is achieved in a vacuum or a protective atmosphere.

In 1963, Dring discussed the results of research to bond alumina-to-molybdenum and alumina-to-niobium seals by diffusion for service up to 1500° C (ref. 104). Two approaches were used during this study: (1) The formation of seals between a metal and a ceramic, and (2) the formation of seals between a metal and the metallized surface of a ceramic. The initial experimental studies were conducted with sheet specimens; however, the joint design shown in figure 11 was used for final evaluation of a bonding technique.

During the study to bond molybdenum or niobium to an unmetallized ceramic, numerous intermediate materials were applied to the joint surfaces to promote diffusion. These were largely ineffective in producing a strong bond

between alumina and molybdenum. However, a 95 percent niobium-5 percent nickel mixture applied to the faying surfaces of the alumina cylinder by plasma-arc spraying techniques was very effective. Dring recommended the following procedures to produce acceptable seals:

1. Dry-lap a circular area on the niobium cap
2. Grit-blast the niobium cap and alumina cylinder
3. Plasma-spray 95 percent niobium-5 percent nickel mixture on the bevelled edge of the alumina cylinder and on the inside of the niobium cap

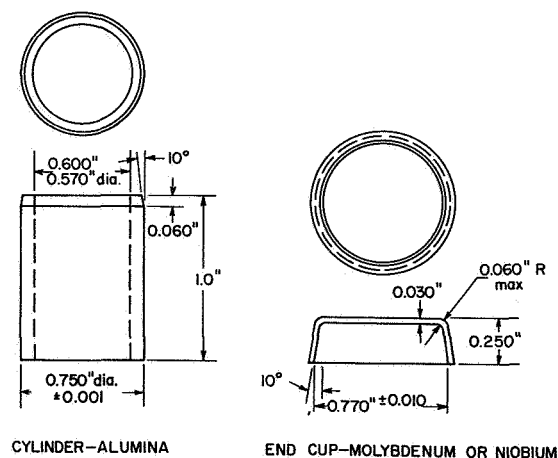


FIGURE 11.—Parts for seal evaluation (ref. 104)

4. Dry-lap cylinder and cap
5. Wet-lap cylinder and cap
6. Assemble joint members
7. Diffusion-bond assembly in a vacuum (10^{-3} torr) for 5 hours at 1524°C (2775°F).

Mechanically strong seals were also produced between molybdenum sheet and the metallized surface of a high-purity alumina body. An alumina cylinder was first metallized with a layer of 85 percent molybdenum-10 percent manganese-5 percent titanium hydride. After this layer was sintered to the alumina cylinder, a second metallizing layer was slurry-coated to the ceramic surface and fired; the composition of this layer was 80 percent molybdenum-20 percent chromium. The faying surfaces of the molybdenum sheet and metallized alumina ceramic were then lapped and the joint members assembled. Joining proceeded in a dry argon atmosphere at 1800°C (3272°F). While joints made in this manner had acceptable strength properties, it was necessary to infiltrate the metallized ceramic with a manganese oxide-alumina eutectic mixture before bonding to obtain hermetic sealing.

Metelkin, Makarkin, and Pavlova, in investigating the diffusion bonding of ceramic-to-metal joints (ref. 111), developed bonds between copper and a variety of ceramic materials such as alumina (72.0, 94.0, and 99.5 percent), sapphire, forsterite, and steatite. The joints were produced in a vacuum as well as a hydrogen atmosphere under the following conditions: pressure 14.4 psi; temperature 1000°C (1832°F); and time 10 minutes. The specimen used for the studies was a copper disk (0.012 to 0.020 inch thick) sandwiched between two ceramic cylinders (0.52-inch O.D., 0.100-inch I.D., and 1.8 inches long). The strongest joints between these materials were obtained in a hydrogen atmosphere; the joints generally failed in the ceramic.

Additional joints were made between a 99.5-percent alumina body and the following metals: stainless steel, Kovar, nickel, palladium, titanium, Nichrome, low-alloy steel, and iron. The bonding conditions were the same as noted above except the temperature was increased to 1250° to 1300°C (2282° to 2372°F). Satisfactory joints were obtained between all of

these ceramic-to-metal combinations. When joints between alumina and several refractory metals were attempted, bonding did not occur either in a vacuum or in hydrogen; however, satisfactory joints were obtained when a ductile metal such as copper, nickel, and stainless steel was used as an intermediate material between the metal and ceramic surfaces.

Also studied during this investigation were the effects of hydrogen dewpoint, ceramic grain size, time, pressure, and temperature on the strength of ceramic-to-metal joints. Maximum joint strength was obtained at about 28 psi when the joints were held at temperature for 10 to 15 minutes; however, joint strength increased at high temperatures because the reaction processes are temperature-dependent. The dewpoint of the hydrogen atmosphere also affected joint strength, maximum joint strength was obtained with a dewpoint of about 40° to 45°F . Thus, water vapor provided oxygen for metal-oxide formation.

During an early investigation conducted in the late 1940's, Wellinger (ref. 112) discussed the fabrication of diffusion-bonded joints between copper and steatite and noted that the bonding time required to join these materials at 1000°C (1832°F) with a pressure of 3000 psi was about 2 hours. The bonding time was reduced to 10 minutes if the copper surface was covered with a thin layer of cuprous oxide.

Diffusion bonding may also have taken place in the so-called "ram seal" or "crunch seal" that has been developed by a division of the Radio Corporation of America (ref. 113). However, the mechanism of joining is probably cold pressure welding. High-alumina ceramic cylinders, up to 20 inches in diameter, are ground to a blunt bevel on the end. Then, a copper-plated tool steel cylinder whose inner diameter is smaller than the outer diameter of the alumina cylinder is pushed onto the ceramic cylinder under considerable pressure to produce a room-temperature seal. This metal-to-ceramic seal can be used at temperatures up to 550°C (1022°F) and heat-cycled repeatedly.

Ultrasonic Welding

Ultrasonic welding is a solid-state bonding

process for joining metals by introducing high-frequency vibratory energy into overlapping workpieces. For joining metals ultrasonic welding has several advantages over other joining methods:

1. Since thermal distortion does not occur, close dimensional tolerances in an assembly can be maintained.
2. A variety of dissimilar metal combinations can be joined.
3. Thin sheet stock can be joined to much thicker metallic sections.

Care must be used in selecting and applying this process. Problems have been experienced with microcracking during the ultrasonic welding of heat-resistant alloys and some dissimilar metal combinations. Ultrasonic welding has been used most extensively in the electronics industry to join components made from aluminum and copper alloys.

Scheffer, Liederbach, Pikor, and Miller (ref. 114) used ultrasonic joining techniques to produce a hermetically sealed transistor package. The base of the package was a 94- to 96-percent alumina wafer that measured 0.310 by 0.310 by 0.030 inch. The required seal and terminal patterns on the ceramic wafer were provided by moly-manganese metallizing. After metallizing, the patterns were nickel- and copper-plated and then solder-dipped. The transistor was mounted in a cavity in the ceramic wafer. After assembly, a brass cap was soldered to the wafer to produce a sealed unit. Since a flux could not be used because of the danger of contaminating the ultrasensitive transistor surface, ultrasonic methods were used for joining. A special ultrasonic sealing press was constructed to position the seal components and isolate the soldering tip from any physical connection except to the transducer; the soldering tip was heated by means of an isolated annular heater. Joining was accomplished successfully without a flux.

Dring investigated ultrasonic welding during a study to develop techniques to produce ceramic-to-metal seals for thermionic converter applications (ref. 104). The object of the research was to join 0.001-, 0.005-, and 0.025-inch-thick molybdenum sheet to a moly-manganese metallized alumina ceramic. Although some progress was made in producing single spot

welds between the molybdenum sheet and the metallized ceramics, the results were not reproducible enough to proceed with the second-phase operation—the production of overlapping welds. The most suitable joints were made when a tantalum foil was placed between the molybdenum sheet and the ceramic.

High-Energy Welding With Exploding Foils

Vagi and DeSaw conducted an investigation to obtain information on the requirements for joining metals, nonmetals, and metals to nonmetals with exploding foils (ref. 115). In this method, a metal foil is positioned between the two parts to be joined. Then, the foil is exploded by passing a large current through it from a bank of capacitors. Under the proper conditions, joining will occur. Exploding foils behave similar to exploding wires when a large current is passed through them.

Most joining experiments were conducted using a 0.125-inch-wide, 0.001-inch-thick tantalum foil sandwiched between the abutting ends of 0.125-inch-diameter rods; some studies were also made with a reduced center-section type of foil (fig. 12). The rods to be joined were held in place with a modified spot-welding head. Quartz-to-quartz joints were made under the following conditions: preset clamping force 19.5 pounds; charging voltage 5 kilovolts; and capacitance 145 microfarads. The joint efficiency of these bonds was 30 percent. In attempts to join tungsten to quartz under the same welding conditions, the tantalum foil was bonded to the tungsten rod after the explosion but bonding to the quartz rod did not occur. Experiments to join other materials were also conducted, and the authors reported that:

1. The exploding-foil process appears promising for bonding a variety of materials, such as quartz, Fiberglas tape, phosphor-bronze woven tape, and thin-wall zirconium tubing.
2. Metal coatings were produced on the facing surfaces of alumina and graphite.
3. Consistent and continuous edge welds were obtained with metal specimens. This edge-fusion effect was used to join thin-wall tubing.
4. Exploding-foil welding variables must be closely controlled; they include: part material,

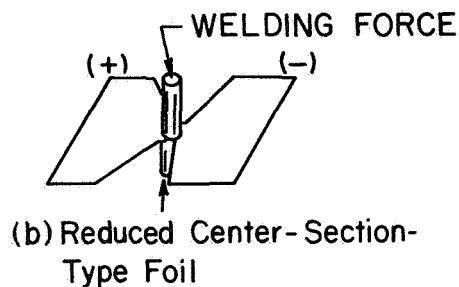
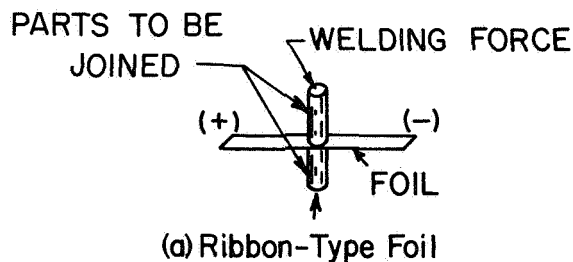


FIGURE 12.—Arrangement of foils and parts for bonding with exploding foils

size, and shape; foil geometry and thickness; capacitor voltage and discharge time; welding-force magnitude and alignment of parts; and the reaction of the parts during welding.

Electroforming

Electroforming—a process in which a layer of metal is deposited on a surface or form by electroplating—has been investigated as a method to fabricate ceramic-to-metal joints. After plating, the form is removed to leave a shell of metal whose inside configuration matches that of the form. Hare, of the Stanford Electron Devices Laboratory, studied this joining process in connection with the fabrication of an external-circuit traveling-wave tube that consists of a large number of ceramic-to-metal seals (ref. 116). Hare lists the following steps in producing an electroformed seal:

1. Metallize the ceramic in accordance with the moly-manganese process
2. Plate the metallized surfaces with nickel and sinter
3. Plate the nickel surface with copper and sinter

4. Plate the copper surface with gold
5. Assemble the ceramic-to-metal joint. Make provisions for electrical contact to the metal and metallized surfaces
6. Mask-off any electrically conductive areas not to be plated
7. Clean joint assembly and plate with copper.

Typical joint designs evaluated in this program are shown in figure 13. The initial current density in the electroplating bath was 40 amperes/square foot for 30 seconds; then, the

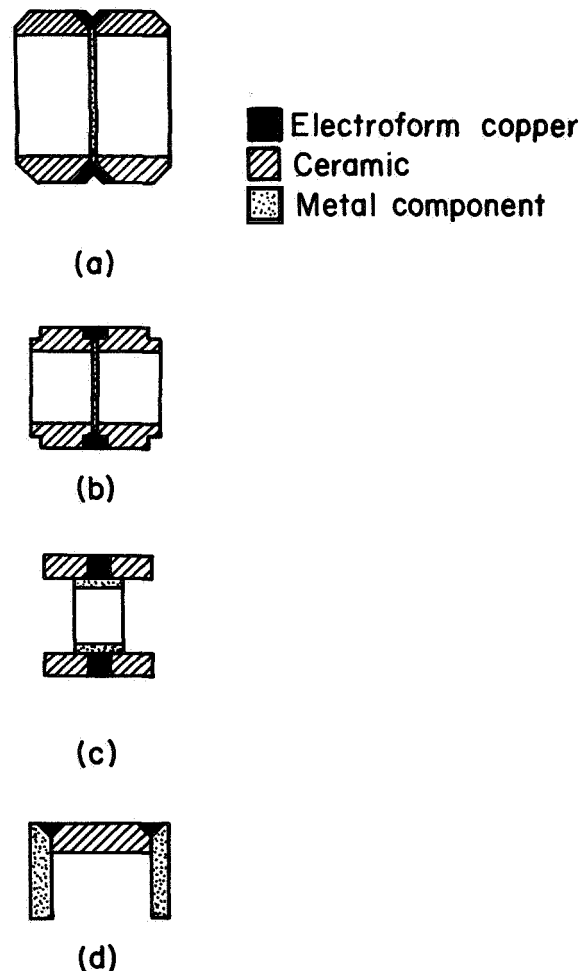


FIGURE 13.—Joint designs for electroformed seals (ref. 116). (a) Vee design of metal-to-ceramic electroform seal; (b) step design of metal-to-ceramic electroform seal; (c) step design using plain ceramic cylinders and metal sleeves; (d) vee design using ceramic disk and metal cylinder

current density was reduced to 10 amperes/square foot. At this level the deposition rate was 0.008 to 0.010 inch in 24 hours. Using the joint design shown in figure 13(b), an assembly of 41 stacked seals was joined by electroplating. The metals used in the electroformed seals included molybdenum, copper, and Kovar (it should be possible to use other structural metals); the ceramic was a high-alumina body.

Hare stated that electroforming is useful where glass windows for electronic devices may be damaged by a high-temperature sealing operation, where sapphire or quartz must be used in seals, and where a large, expensive ceramic-to-metal seal must be made.

In a program to develop ceramic-to-metal seals for thermionic converters, Dring evaluated the electroforming technique (ref. 104). Attempts to join molybdenum to a metallized alumina ceramic by rhodium-electroplating were inconclusive because of the difficulty in plating molybdenum.

Reed and McRae used electroformed iron, overplated with chromium, to produce a seal between niobium or Kovar to metallized alumina (ref. 117) to be used in a liquid-metal environment.

SOLID-LIQUID PHASE JOINING

Soldering

Soldering is a process in which metals are joined below 800° F by using a nonferrous filler metal or solder. The solder is distributed throughout the joint by capillary attraction, provided the proper clearances exist between the joint surfaces. The solder and the base metal are bonded by adhesion and physical attachment; however, sometimes a thin layer of the base metal is dissolved by the solder and an intermetallic compound forms to aid in bonding. The ease with which the solder wets and flows on the base metal surface is a measure of the metal's solderability.

Soldering has long been used in the electrical industry to join glass and ceramic parts to metals. Since it is a low-temperature joining process, there are limitations on the service temperature of soldered joints. While other solders are used occasionally for special joining

applications, most electrical joints are made with tin-lead solders having a tin content of about 60 percent. The solders have excellent wetting and flow characteristics, are quite ductile, and have compositions that approach the eutectic in the tin-lead system, which occurs at about 63 percent tin. Since the solders begin to melt at 361° F, the service temperature of the soldered joint is 200° F or less. Soldered ceramic-to-metal joints are used in electrical insulators, feedthroughs, and contacts on electronic components.

Metallizing is necessary to ensure the solderability of ceramic surfaces. Such surfaces are usually metallized by thermally reducing metal salt solutions and sintering paints composed of precious metal flakes or powders in an organic binder to which a glass frit has been added. (These metallizing procedures were discussed in chapter 3.) Solders are also occasionally used to join a metal to an electroplated ceramic surface metallized by the moly-manganese process. However, this process is best suited for high-temperature applications and its high cost may not be justified for soldering.

Many reports of soldering glass and ceramic-to-metal joints can be found in the literature. In 1949, Jenny discussed the fabrication of soldered ceramic-to-metal seal using the techniques that had been developed for cable terminals, bushings, and connectors (ref. 118). As shown in figure 14, soldered joints should provide flexibility to the joint and minimize the load that must be supported by the solder. To minimize stresses in the ceramic, the metal member should be relatively thin and located on the outside of a cylindrical joint. Jenny recommended the use of tin-lead solders containing silver to minimize dissolution of the thin silver metallizing film; short soldering times were suggested for the same reason. Jenny also provided creep data for common solders.

Bondley discussed the use of low-melting soft solders with the titanium hydride process used to ensure the wettability of ceramic surfaces (ref. 119). However, a dam or well must be provided to hold the solder in place during the interval between melting of the solder and dissociation of the titanium hydride. Bondley also reviewed the characteristics of solders based on

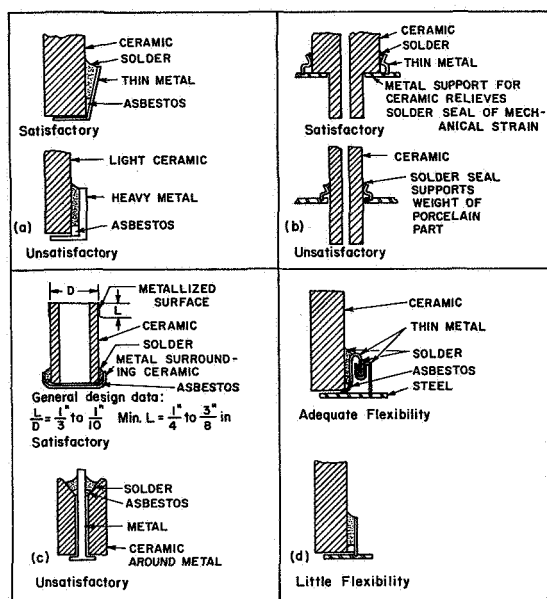


FIGURE 14.—Designs for soldered joints (ref. 118)

tin, lead, and indium. Experimental solders were prepared and evaluated by soldering two 1/2-inch-diameter ceramic rods together and testing them in flexure by four-point loading; 70-percent joint efficiencies were obtained. The solders were based on lead with additions of 0 to 50 percent silver, 0 to 50 percent indium, and 0 to 5 percent copper.

In 1955, McGuire of the Los Alamos Scientific Laboratory reported on a method to tin the surfaces of metals and nonmetals for subsequent joining operations (ref. 120). He found that an abrasive wheel on a hand grinder could be loaded with a solder by holding a stick of the solder against the rotating wheel. When the loaded abrasive wheel was rotated in contact with a metal surface, the frictional heat melted the solder and, at the same time, friction removed the surface oxides from the metal. The solder immediately wet the cleaned surface and flowed. This technique made it possible to solder a copper electrode to a tinned aluminum surface. The process was further evaluated by tinning other metals (stainless steel, titanium, and many of the refractory metals that are difficult or impossible to solder by conventional means). Soft and hard glasses as well as several ceramics were also tinned in this manner. For example,

a fired magnesium oxide body was tinned with a mixture of Wood's Metal* and 50Sn-50In solder; joints were made later with a 50Sn-50Pb solder.

Brazing

Brazing is uniquely suited to fabricating ceramic-to-metal joints and seals, and despite recent advances in the technology of metals joining, its position as the foremost method of making such joints has not been threatened seriously. In many respects brazing and soldering are similar processes; in both instances, the materials to be joined are heated and joined by a filler metal whose melting temperature is below those of the base materials. The four important differences distinguishing these processes are discussed below.

Brazing proceeds at temperatures above 800° F (430° C), while soldering proceeds below 800° F. Filler metals for soldering are based on such low-melting metals as tin, lead, and indium. Brazing filler metals are based on the noble metals, the heat-resistant metals such as nickel and cobalt, certain reactive metals such as titanium, beryllium, and zirconium, and the refractory metals.

In brazing, as in soldering, the filler metal is distributed throughout the joint area by capillary attraction; however, the clearances between the joint surfaces are more critical because of the reactions occurring during brazing. The recommended joint clearances are determined by the characteristics of the base and filler metals; data on clearances can be found in the *Brazing Handbook* and in the *Welding Handbook*, both published by the American Welding Society. (Certain so-called "wide gap" filler metals have been developed for use where joint clearances cannot be maintained.)

In soldering, the mechanisms responsible for joining are associated with adhesion and physical attraction, although a slight reaction along the joint interface may occur. Since brazing is conducted at high temperatures, the major bonding mechanisms are reactions between the base metals and filler metal, diffusion of the base

*25Pb-50Bi-12.5Cd-12.5Sn.

metal and filler metal constituents across the joint interface, and the formation of intermetallic compounds. The magnitude of these reactions depends on many factors such as the materials being joined, the filler metal, and the brazing cycle.

Soldering is usually done in air using a flux. While fluxes are suitable for low-temperature brazing, they lose their effectiveness at elevated temperatures, requiring other means of protection. The protective environment significantly affects the soundness and properties of the brazed joints. Controlled atmospheres are used to prevent oxidation of the joint materials, reduce surface oxides, or in some cases, produce limited oxidation. Oxide reduction depends on the type of gas, the gas dew point, and the brazing temperature. Vacuum environments also provide oxidation resistance. The filler metals used for vacuum brazing must be selected with care to avoid evaporation. Surface films and oxides are also removed in a vacuum, but the mechanism of removal is not well defined. Finally, the effects of gaseous atmospheres on base metal must be considered. For example, the properties of the reactive and refractory metals are adversely affected by even small traces of gaseous contaminants.

Thus, brazing is a much more critical operation than soldering; extensive knowledge is necessary to select the proper process, filler metal, atmosphere, and brazing cycle.

Although the metallizing of ceramic surfaces is costly and time-consuming, the brazing of metals to such surfaces is a straightforward operation because the metallizing layer ensures wettability of the ceramic by the filler metal. However, certain metals and their hydrides possess the ability to wet bare ceramic surfaces, and "active hydride" and "active metal" processes based on this property have been developed for producing ceramic-to-metal seals and joints.

The joining of ceramics to metals with the active metal or active hydride processes dates back to the middle 1940's when Bondley of the General Electric Company announced the use of titanium hydride for this purpose (ref. 121). Bondley painted the area to be joined with a

mixture of fine titanium-hydride powders (300 mesh) suspended in a suitable binder. After drying, the ceramic and metal parts were assembled with a silver-base filler metal in contact with the hydride area. The assembly was heated to 900° to 1000° C (1652° to 1832° F) in a vacuum or in a very pure hydrogen atmosphere. As the titanium hydride dissociated, a residue of pure titanium remained on the ceramic surface; the hydrogen evolved in the atomic state during heating and tended to reduce oxides on the material surfaces. When the filler metal melted, it alloyed with titanium to form a silver-titanium alloy that bonded strongly with the metal and the areas of the ceramic that were coated with titanium hydride.

Pearson and Zingesser, in studying the bonding of ceramics with active metals and their hydrides (ref. 122), extended the work of Bondley and found that hydrides of zirconium, tantalum, and niobium were just as effective as titanium hydride in ceramic-to-metal joints. The effectiveness of various filler metals in making bonds with alumina, synthetic sapphire, beryllia, and thoria (table 13) was evaluated. In addition, Pearson and Zingesser found that titanium and zirconium, produced in reducing titanium and zirconium hydride, could also be used in powder form for ceramic-to-metal joints, thus marking the beginning of the "active metal" joining process. In developing experimental filler metals, Pearson and Zingesser noted that excellent bonds to ceramics, diamonds, sapphires, and other materials were made with an alloy containing 85 percent silver and 15 percent zirconium; aluminum-zirconium, aluminum-silver-zirconium, and silver-titanium alloys were also produced and evaluated. The effect of various brazing environments was also investigated, and a vacuum or a controlled atmosphere of hydrogen or an inert gas were employed to produce ceramic-to-metal joints.

In the early 1950's, research was conducted to further develop the active metal and active hydride processes. In 1951, Kelley received a patent on the use of a titanium or zirconium hydride mixture plus copper, silver, and gold for bonding ceramics (ref. 123). Hume applied the same principles to form a hermetic seal be-

TABLE 13.—*Evaluation of Metal Hydrides for Ceramic-to-Metal Joints*

[From ref. 122]

Material	Hydride	Brazing alloy	Atmosphere	Bond	Results
Aluminum oxide.....	ZrH	Pure silver.....	Vacuum.....	Good	Bonded to tantalum Heated to about 1700° C
	ZrH	Pure aluminum.....	Vacuum.....	Good	
	ZrH and TiH	None.....	Vacuum.....	Good	
	TiH	Cobalt.....	Vacuum.....	Good	
Synthetic sapphire...	TiH	Pure silver.....	Vacuum.....	Good	
	ZrH	Pure silver.....	Vacuum.....	Good	
	TaH	Pure aluminum.....	Vacuum.....	Good	
	CbH	Pure aluminum.....	Forepump vacuum...	Good	
	ZrH	Pure silver.....	Dry tank N ₂	Good	
	None	15 percent zirconium- silver alloy.	Forepump vacuum...	Good	
Beryllium oxide.....	ZrH	Pure silver.....	Vacuum.....	Good	Bonded to molyb- denum
	ZrH	Pure aluminum.....	Vacuum.....	Good	
	CbH	Pure aluminum.....	Forepump vacuum...	Good	
	TaH	Pure aluminum.....	Forepump vacuum...	Good	
	None	15 percent zirconium- silver alloy.	Forepump vacuum...	Good	
Thorium oxide.....	ZrH	Pure silver.....	Vacuum.....	Good	
	CbH	Pure aluminum.....	Forepump vacuum...	Good	
	TaH	Pure aluminum.....	Forepump vacuum...	Good	
	None	15 percent zirconium- silver alloy.	Forepump vacuum...	Good	

tween an aluminum bushing and an alumina header (ref. 124). The ceramic header was coated with a suspension of zirconium hydride, a ring of pure silver was placed in the area to be metallized, and the assembly was heated to about 1100° C (2012° F). The zirconium hydride was reduced to elemental zirconium at 500° C (932° F); the zirconium wet the ceramic surface. When the silver melted, it alloyed with the zirconium and coated the ceramic surface. After the assembly cooled, the aluminum bushing was positioned, and the assembly was reheated until the aluminum melted and formed a seal with the metallized ceramic header.

Since these early investigations, joining ceramics to metals by the active metal or active hydride process has advanced significantly. The strengths of joints made by this process are as great as those obtained with joints made by the moly-manganese process. Some difficulty has been experienced in making seals by the active

metal or active hydride process in dry hydrogen. The dew point of hydrogen must be extremely low to prevent oxidation of titanium. According to Chang, the dew point of hydrogen must be about -85° C (-121° F) to reduce titanium oxide at 1000° C (1832° F); such a dew point is difficult to achieve except under laboratory conditions (ref. 125). Producing ceramic-to-metal seals in a vacuum is advantageous in that the parts are outgassed during brazing.

The characteristics of the moly-manganese, active metal, and active hydride processes are summarized in the following paragraphs:

The moly-manganese process is a multi-step sealing process in which the ceramic surface is metallized and plated with one or two metals before brazing can take place. The operations are conducted at a high temperature in a controlled atmosphere of hydrogen; hydrogen firing may discolor some ceramics and produce conductive surfaces. Despite the number of steps

required to produce a seal, the moly-manganese process can be automated quite readily, and minor deviations in the process variables can be tolerated.

The active hydride process is essentially a single-step process in which hydride reduction and brazing proceed simultaneously. Joining in a vacuum or in a controlled atmosphere of hydrogen or an inert gas is accomplished at relatively low temperatures, permitting a fast brazing cycle. This process is more difficult to automate than the moly-manganese process, particularly if the joints are produced in a vacuum. Careful control must be exercised in coating the ceramic with the hydride.

The active metal process may be a one-step operation like the active hydride process.* Joining proceeds at high temperatures in a vacuum or in a controlled atmosphere; vacuum joining is not readily automated.

These processes will be discussed further from the application standpoint in the following sections, with emphasis on recent or current research.

Brazing to Metallized Ceramic Surfaces

The technology of joining metals to metallized ceramic surfaces was first applied on a large scale by the electronics industry. Since numerous reports and papers have been prepared on fabricating vacuum-tube components by these methods, only some especially interesting developments will be discussed here.

In the early 1950's, Coykendall of the Machlett Laboratories discussed the procedures used to assemble a UHF power triode designed to operate in the 30- to 2000-megacycle range (ref. 126). Ceramic-to-metal seals as large as 7 inches in diameter were made by brazing nickel-iron rings to cylindrical alumina sections; the ceramic parts were metallized by the moly-manganese process. The joints were brazed with pure silver, so that other, lower melting silver-base alloys could be used for subsequent joining operations. Cronin has discussed the trends in the design of ceramic-to-metal seals for use in

high-power magnetrons (ref. 127). LaForge has prepared an excellent review of the procedures to fabricate seals for high-power pulsed klystrons delivering a peak power output of 30 megawatts at an average power of 30 kilowatts (ref. 63). The authors discussed features of the klystron and the requirements for ceramic windows that provide vacuum sealing for the output wave guide while permitting passage of electromagnetic energy. At first, the high-alumina window sections were metallized with moly-manganese and brazed with either the 82Au-18Ni or 72Ag-28Cu filler metals. The metallized layer was nickel-plated when the silver-copper eutectic alloy was used. The wettability of 95- to 97-percent alumina bodies was improved with an activated metallizing mixture containing molybdenum, manganese, iron, calcium oxide, and silicon oxide.

Two important programs to develop high-temperature seals for vacuum tubes were conducted by the Sperry Gyroscope Company and the Radio Corporation of America (refs. 128 and 129). Engineers at Sperry investigated the effect of process variables (metallizing composition, powder particle size, metallizing layer thickness, method of application, composition of alumina ceramic body, and sintering time and temperature) on the strength and reproducibility of brazed assemblies. The RCA study was concerned with developing ceramic-to-metal sealing techniques that could be used in producing output windows for high-power microwave tubes that would withstand a 700° C (1292° F) bake-out temperature. Procedures were developed to metallize synthetic sapphire (pure alumina), and adherence tests showed that optimum metallizing was achieved with a mixture of 80- to 90-weight percent molybdenum and 10- to 20-weight percent S-641A (a proprietary material that resembles steatite). The studies also included suitable filler metals for ceramic-to-metal seals (table 14). The 62.5 Cu-37.5 Au alloy, which appeared to meet the temperature requirements, was further evaluated to determine the effect of metallizing variables on the strength of synthetic sapphire joints. The joints were made by metallizing sap-

*A thin metallized layer of titanium or molybdenum on BeO surfaces has enhanced wetting.

TABLE 14.—*Evaluation of Brazing Filler Metals for Joining Synthetic Sapphire Metallized With Molybdenum and S-641A Mixtures*

[From ref. 129]

Metallizing material, percent	Brazing material, percent	Brazing tempera- ture, °C	Quality	Penetration	Remarks
80 Mo, 20 S-641A*	Copper	1090	Good	Slight	
90 Mo, 10 S-641A	Copper	1090	Good	Very slight	
80 Mo, 20 S-641A	37.5 gold 62.5 copper.	1025	Fair	Slight	
90 Mo, 10 S-641A	37.5 gold 62.5 copper.	1025	Excellent	Very slight	Excellent structure.
80 Mo, 20 S-641A	50.0 gold 50.0 copper.	1005	Fair	Slight	
90 Mo, 10 S-641A	50.0 gold 50.0 copper.	1005	Excellent	None	
90 Mo, 10 S-641A	35.0 gold 62.0 copper. 3.0 nickel.	1035	Fair	Slight	
80 Mo, 20 S-641A	35.0 gold 62.0 copper. 3.0 nickel.	1035	Excellent	Slight	
90 Mo, 10 S-641A	82.0 gold 18.0 nickel.	960	Fair	None	
80 Mo, 20 S-641A	82.0 gold 18.0 nickel.	960	Excellent	None	

*S-641A—a proprietary material that resembles steatite.

phire rods 0.625 inch long and 0.250 inch in diameter and brazing them in pairs. Two small specimens with a cross-sectional area of 0.0049 square inch were machined from each brazed rod and tested; the seal strength data are summarized in table 15. Attempts to metallize synthetic sapphire with tungsten mixtures were discontinued because the seal strength obtained with tungsten-metallized sapphire did not match that obtained with molybdenum metallizing mixtures. Procedures were also developed to metallize and braze beryllia (table 16), and synthetic sapphire and beryllia output windows were fabricated and evaluated. Usually such windows are made by brazing a metallized ceramic disk to a machined ring; however, because voids were encountered, a subassembly consisting of a copper (or copper-gold) ring cast onto the ceramic disk was produced (fig. 15(a)). This assembly was machined to precise dimensions and brazed to the outer copper

sleeve as shown in figure 15(b). Output windows of this type withstood the required 700° C (1292° F) bake-out temperature and passed the thermal cycling test (1000 cycles between 20° and 125° C or 68° and 258° F).

Several research programs have been conducted to develop sealing techniques for constructing energy-converter devices. In 1964, Bristow, Grossman, and Kaznoff developed mixtures composed of 60- to 70-percent molybdenum powder and 30- to 40-percent oxides of aluminum, calcium, magnesium, and yttrium for metallizing high-alumina ceramics (ref. 11). (The results of studies to evaluate these metallizing mixtures were discussed earlier in the section on "Metallizing.") During the course of this program, vacuum-tight seals were produced between alumina and molybdenum, tantalum, and niobium. Goldstein has described the fabrication of ceramic-to-metal seals for spaceborne reactor components (ref. 130). The seals were

TABLE 15.—*Seal Strength Data on Synthetic Sapphire Joints*

[From ref. 129]

Metallizing mixture, percent	Firing time, hours	Firing temp, °C	Plating material	Brazing material, percent	Modulus of rupture, psi			Failure location
					Average	High	Low	
80 Mo.----- 20 S-641A.*	0.5	1500	Nickel.-----	37.5 Au.---- 62.5 Cu.	36 300	54 000	26 500	Metallizing layer.
90 Mo.----- 10 S-641A.	0.5	1700	Nickel.-----	37.5 Au.---- 62.5 Cu.	43 700	48 000	39 000	Random: Sapphire. Sapphire-metallizing interface.
95 Mo.----- 5 S-641A.	0.5	1800	Nickel.-----	37.5 Au.---- 62.5 Cu.	41 900	47 500	36 300	Random: Sapphire-metallizing interface. Sapphire.
90 Mo.----- 10 S-641A.	0.5	1600	Nickel.-----	37.5 Au.---- 62.5 Cu.	40 400	45 600	39 000	Random: Sapphire-metallizing interface. Sapphire.
90 Mo.----- 10 S-641A.	0.5	1750	Nickel.-----	37.5 Au.---- 62.5 Cu.	47 000	51 400	37 900	Sapphire.
92.5 Mo.----- 7.5 S-641A.	0.5	1750	Nickel.-----	37.5 Au.---- 62.5 Cu.	34 500	49 300	12 800	Random: Metallizing and metallizing-sapphire interface.
92.5 Mo.----- 7.5 S-641A.	0.5	1800	Nickel.-----	37.5 Au.---- 62.5 Cu.	42 300	46 300	39 600	Sapphire.
90 Mo.----- 10 S-641A.	2.0	1750	Nickel.-----	37.5 Au.---- 62.5 Cu.	47 400	55 900	33 300	Random: Sapphire. Sapphire-metallizing interface.
90 Mo.----- 10 S-641A (fine ink).	0.5	1700	Nickel.-----	37.5 Au.---- 62.5 Cu.	45 200	50 900	42 300	Sapphire.

* S-641 A—a proprietary material that resembles steatite.

NOTE: Modulus-of-rupture figures are influenced by the strength of the sapphire used, which may vary between 25 000 and 60 000 psi with no visible cause for the variance. All samples with breaks in the sapphire lower than 37 000 psi were deleted from calculations.

required to withstand operating temperatures of 1000° C (1832° F), be resistant to high-temperature cesium vapor, and possess adequate resistance to thermal cycling. To meet these requirements, a metallized 97-percent alumina ceramic was brazed to niobium with vanadium as the filler metal. Dring of the Bendix Corporation also conducted studies to produce ceramic-to-metal seals for a cesium-vapor-filled thermionic converter (ref. 104). A 99.5-percent alumina body, metallized with a molybdenum-titanium mixture, was brazed to molybdenum with the following filler metals: nickel, nickel-iron, cobalt, and iron. Sound joints were ob-

tained with cobalt and iron, but the thermal-expansion coefficient for these metals accentuated the expansion mismatch between the molybdenum metal member and the alumina ceramic, causing gross cracking. Additional seals were made between alumina and niobium using pure palladium as the brazing filler metal. Niobium was used instead of molybdenum to improve the expansion match between the ceramic and metal joint members. For this seal, the alumina body was metallized with a tungsten-yttria mixture. Vacuum-tight seals were produced but precise temperature control during brazing was imperative, since the filler metal tended to erode the

TABLE 16.—*Seal Strength Data on Beryllia Joints*

[From ref. 129]

Metallizing mixture, percent	Metal-lizing time, hour	Firing temperature, °C.	Plating material	Brazing material, percent	Modulus of rupture, psi			Failure location
					Average	High	Low	
100 Molybdenum (fine).	0.5	1550	Nickel.....	37.5 Au..... 62.5 Cu.	26,400	30,600	20,000	Random metal-lizing layer.
90 Molybdenum, 10 S-641A* (fine).	0.5	1600	Nickel.....	37.5 Au..... 62.5 Cu.	33,100	38,000	27,100	90 percent in ceramic; 10 percent random.

*S-641A—a proprietary material that resembles steatite.

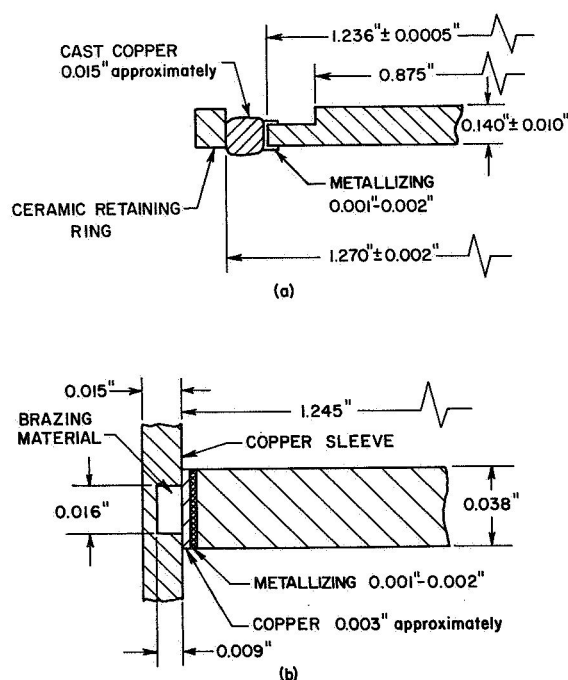


FIGURE 15.—Design and assembly of brazed synthetic sapphire and beryllia output windows (ref. 129). (a) Subassembly for output windows; (b) brazed output windows (enlarged section)

niobium. To overcome the problem, Dring suggested the use of the niobium-palladium eutectic alloy for brazing.

In another program to design and construct equipment for the direct conversion of nuclear to electrical energy, engineers at the Los Alamos

Scientific Laboratory developed ceramic-to-metal seals for use at 1000° C (1832° F) in a cesium vapor environment (refs. 103 and 131). The seal materials also had to be resistant to radiation damage. The basic cell for energy conversion consists of a nuclear fuel element that acts as an electron emitter, a metal base section to which the fuel element is attached, and a metal electron collector section; the inner space of the cell is filled with cesium vapor. Ceramic-to-metal seals are required to isolate the cell's base and collector sections. A schematic of the basic thermionic converter cell is shown in figure 16. The base and collector sections were machined from Nb-1Zr; silica-free alumina was selected for isolating the sections. In 1963, Brundige and Hanks discussed the procedures to produce the ceramic-to-metal seals (ref. 103). Several high-alumina ceramics were metallized with tungsten in accordance with procedures developed by Cowan and Stoddard (ref. 92). Two joint designs were used to make the ce-

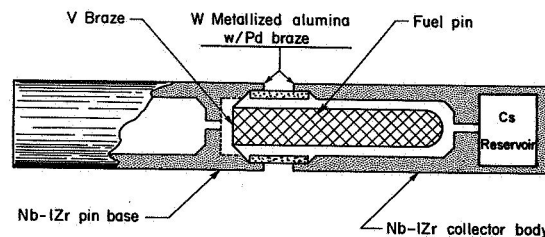


FIGURE 16.—Schematic of basic thermionic converted cell (ref. 103)

ramic-to-metal seal; figure 17(a) shows the seal brazed with the 65Pd-35Co filler metal in the form of washers or rings. In the second design (fig. 17(b)) the filler metal was plated on the metallized ceramic before assembling the joint; palladium and cobalt were electrodeposited in alternate layers to the approximate composition 65Pd-35Co. The resulting joints were leaktight but unreliable. In an extension to this program, Hanks, Kirby, and LaMotte evaluated several filler metals using the joint design shown in figure 17(c); the joints were brazed in a cold-wall vacuum furnace at 10^{-4} torr (ref. 131). These

data are summarized in table 17. While brazing with palladium and vanadium filler metals was satisfactory, some erosion of the base metal occurred. This problem was largely eliminated by using induction heating to produce a very short brazing cycle. Kirby and LaMotte also report on research to evaluate other filler metals, conducted by the Pyromet Company (ref. 132).

Brazing With Active Metals and Hydrides

The concept of fabricating ceramic-to-metal seals by the active metal or active hydride

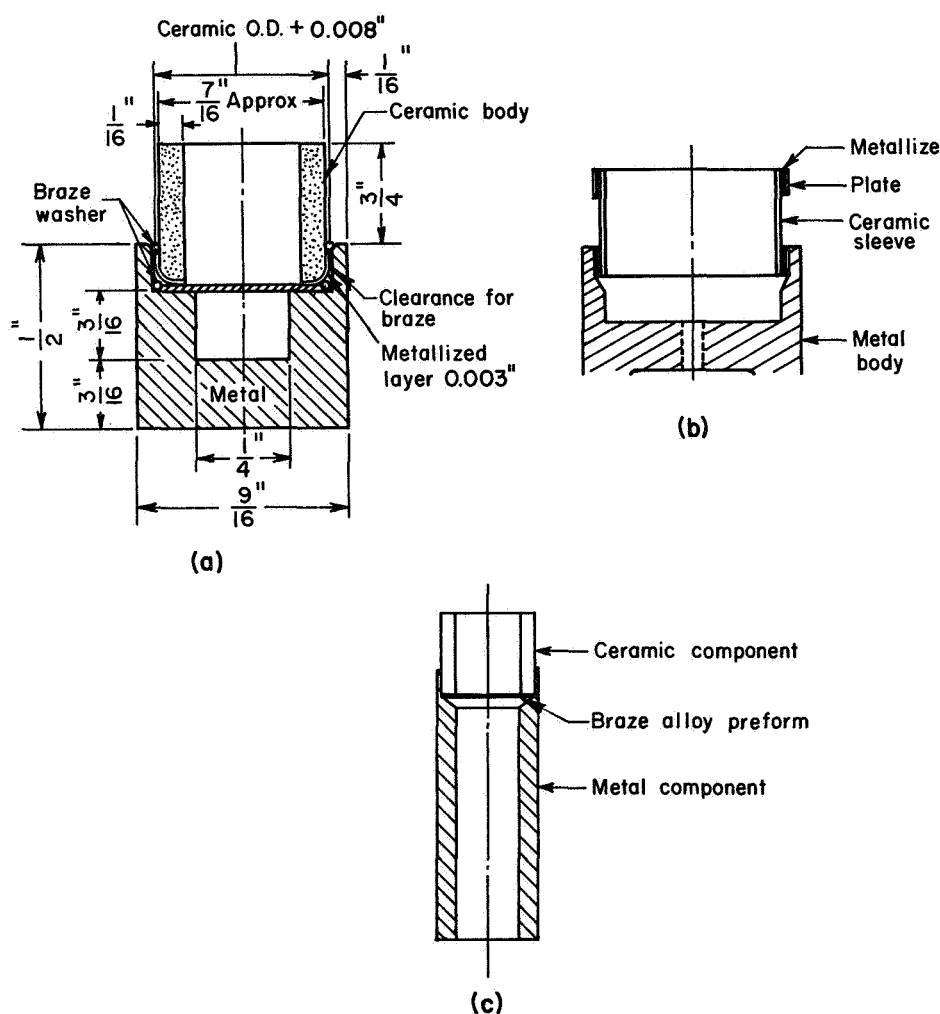


FIGURE 17.—Ceramic-to-metal seals for thermionic converter cells (refs. 103, 131).

(a) Straight seal; (b) plated seal; (c) simplified straight seal

TABLE 17.—*Ceramic-to-Metal Wetting Tests on Metallized Ceramic Surfaces*

[From ref. 131]

Brazing alloy composition, w/o	Ceramic ^a type	Brazing temperature, °C	Results
Vanadium.....	Al-14.....	1960	Wet metal and ceramic well. Considerable alloying with metal. No evidence of metallizing after brazing.
Vanadium.....	Lucalox.....	1960	Same as above.
Palladium.....	Al-14.....	1590	Wet metal and metallized ceramic well. Considerable alloying with metal. Metallized coating still intact.
Pd-35Co.....	Al-14.....	1260	Wet metal and metallized ceramic well. Considerable alloying with metal. Metallized coating still intact.
Co.....	Al-14.....	1540	Wet the metallized ceramic well. Extreme alloying with the metal.

^a Ceramic type	Density, percent theo	Composition
Al-14 (pressed).....	93	Al ₂ O ₃ -0.5 w/o Y ₂ O ₃ .
Al-14 (slipcast).....	96	Al ₂ O ₃ -0.5 w/o Y ₂ O ₃ .
Lucalox.....	98	Al ₂ O ₃ -0.3 w/o MgO.

process was first applied in the electronics industry. However, in recent years, these joining processes have found other uses to meet the need for high-temperature vacuum-tight seals in the nuclear and aerospace industries.

In 1954, Bender of Sylvania Electric Products, Inc., discussed research to evaluate the active metal process for joining zirconia ceramics (ref. 133). Specifically, he conducted wetting tests to determine the percentage of titanium that should be added to the silver-copper eutectic alloy (72Ag-28Cu) to obtain maximum wetting in a dry hydrogen atmosphere; alloys with 10 percent titanium produced the best results. He also investigated the silver-zirconium system for joining zirconia and alumina ceramics; good wetting and bonding were observed when the tests were conducted in a vacuum. Evans, of Sylvania, published an article in 1954 discussing the feasibility of using the active metal process to produce typical vacuum-tube seals (ref. 134). The filler metal for this work was the silver-copper eutectic alloy on a titanium wire core. Martin (Edgerton, Germeshausen, and Grier) discussed

research on the active hydride process to seal windows in high-power magnetrons (ref. 135). Joints between alumina and Kovar produced in a vacuum of 10⁻³ torr or lower by painting the ceramic with a suspension of fine titanium hydride and brazing the joint with 72Ag-28Cu filler metal withstood sustained bake-out temperatures of 700° C (1298° F). A ceramic-to-stainless steel bellows joint was also produced by this method. A simplified version of the active metal process has been used successfully by a firm engaged in producing electrical feed-through components for vacuum processing equipment (ref. 136). After the parts are assembled, a band of titanium is painted on the ceramic surface, a ring of 72Ag-28Cu is positioned, and the joint is brazed in a vacuum.

Recently, Fox and Slaughter investigated the use of experimentally developed active metal alloys for producing ceramic-to-ceramic and ceramic-to-metal joints, some of which may be potentially useful in nuclear reactor technology (ref. 12). The filler metals, 68Ti-28Ag-4Be and 49Ti-49Cu-2Be, were originally developed for joining graphite to metal. However, studies in-

licated that good wetting and flow occurred between 49Ti-49Cu-2Be and alumina, beryllia, and uranium oxide; the 68Ti-28Ag-4Be alloy produced good wetting on alumina surfaces but only fair wetting on beryllia and uranium oxide. Several other titanium- or zirconium-base alloys showed promise in wetting oxide ceramics. During the initial studies, sound joints were produced between the following combinations of materials: alumina-to-alumina with 49Ti-49Cu-2Be; alumina-to-Zircaloy 2 with 48Ti-48Zr-4Be; uranium oxide to molybdenum with 49Ti-49Cu-2Be; uranium oxide to niobium with 68Ti-28Ag-4Be; uranium oxide to zirconium with 95Zr-5Be; and beryllia to zirconium with 95Zr-5Be. To demonstrate the possible uses of these active metal alloys for fuel element applications, a compartmented aluminum oxide assembly was vacuum-brazed with the 49Ti-49Cu-2Be alloy; a simulated beryllia fuel bundle was brazed with the same alloy. An alumina-to-titanium bearing assembly and a Hall cell assembly that included joints between synthetic sapphire and zirconium were also fabricated.

In developing ceramic-to-metal sealing techniques for the production of output windows in high-power microwave tubes, engineers at the Radio Corporation of America investigated the active metal and active hydride processes (ref. 129). They evaluated titanium, zirconium, and vanadium foils and hydrides of titanium and zirconium with foils of nickel, copper, and a 37.5Au-62.5Cu used as the brazing materials. Active metal alloys were prepared by combining foils of the active metal with foils of nickel and copper in proportions to produce a eutectic or near-eutectic alloy, wetting tests were conducted, and specimens were prepared to determine the modulus of rupture. The studies indicated that active metal seals can be developed with strengths greater than those currently obtained if an intermediate metal with a low expansion coefficient is introduced into the joint. It was also concluded that ceramics having lower expansion coefficients than alumina probably cannot be joined by the active metal process.

Research to develop a space power alternator

capable of delivering 300 watts electrical power has been underway at the Aerospace Electrical Division of the Westinghouse Electric Corporation since 1960. The power system consists of a nuclear reactor as a heat source, a thermodynamic system to convert thermal energy to mechanical energy, and an alternating-current generator to convert mechanical to electrical energy. Since the generator is connected directly to a potassium-vapor-driven turbine, a bore seal is needed in the rotor cavity to isolate the stator electrical windings from the potassium vapor. The tubular bore seal consists of a thin ceramic section hermetically sealed to metal members at each end. The ceramic-to-metal sealing studies undertaken by the Eimac Division of Varian Associates have been reviewed by Hoop in a recent summary report (ref. 10). Major accomplishments are discussed below.

1. *Tensile tests.*—Studies were conducted to select the ceramic and metal members of the seal as well as a suitable brazing alloy. The test specimens were made by brazing a thin metal section between two halves of the ASTM test specimen, CLM-15. Active metal filler metals that contained substantial amounts of zirconium and titanium were used for most joints; a limited number of specimens were metallized and brazed. These specimens were tested in tension after exposure in potassium vapor for 1000 hours at 1100° F (593° C), 5000 hours at 900° F (482° C), and 10 000 hours at 900° F. On the basis of these studies, a ceramic body having the following composition appeared most resistant to corrosion by potassium vapor: 97 percent alumina, 1.5 percent each of calcia and magnesia, and less than 0.1 percent silica. The most suitable metal was an alloy resembling Kovar and Nb-1Zr. Several filler metals appeared promising.

2. *Subscale tubular bore seals.*—Metal end sections were brazed to 2.5-inch-diameter ceramic cylinders with 83Ti-17Cu, 75Zr-19Nb-6Be, and 68Ti-28V-4Be as filler metals. The assemblies were filled with a measured amount of potassium, evacuated, sealed, and tested for 1000 hours at 1100° F (593° C); all but two of the ten specimens were leaktight after exposure to potassium vapor.

3. *Large tubular bore seals.*—Procedures to braze large tubular bore seals were studied, and the ceramic cylinder used for this work had the diameter (11.5 inches) of the full-scale bore seal; however, it had a heavier wall thickness (0.190 inch) and was shorter (4 inches) than the full-size unit. Seven specimens were brazed in accordance with the procedures shown in table 18. As can be noted, it was difficult to obtain leaktight seals. Since leaktight tensile specimens had been produced with the same joint materials, the cause of the difficulty was investigated. Based on metallographic studies of specimens brazed with the rapid brazing cycle used to produce tensile specimens and the slow brazing cycle used to produce the large bore seal configurations, it was concluded that brittle, intermetallic compounds had formed during the slow heating cycle; some cracks were observed in these microstructures. Titanium-base active metals appeared unsuitable for sealing unless the joint could be heated and cooled rapidly. However, a further test indicated that vacuum-tight seals could be produced with the 75Zr-19Nb-6Be filler metal using slow heating and cooling cycles.

Similar research by Westinghouse is under-

way to select bore seal materials for advanced space power systems where the seals may be exposed to potassium, NaK, or lithium vapors at temperatures from 1000° to 1600° F (538° to 971° C); the accomplishments of this program have recently been reviewed by Kueser (ref. 137).

1. *Materials selection.*—Extensive screening tests were conducted to select the bore seal materials. The performance of several high-alumina ceramics (94 to 100 percent Al_2O_3) and a high-beryllia ceramic (99.8 percent BeO) was evaluated in room-temperature flexural strength tests conducted before and after test bars were exposed to alkali metal vapors at elevated temperatures. The flexural strength of beryllia was not affected seriously by exposure in potassium vapor at 1600° F for 500 hours. Under the same test conditions, the strength of the alumina ceramics decreased sharply as the Al_2O_3 content decreased from 100 to 94 percent. The strength of a 99.7-percent alumina decreased slightly when the ceramic was exposed to potassium vapors at 1000° F for 500 hours; however, it decreased by one-half when exposure occurred in NaK vapor under the same conditions. Little effect on strength was noted when the 99.8-per-

TABLE 18.—*Trial Brazing of 11.5-Inch-Diameter Tubular Ceramics to 0.030-Inch-Thick Nb-1 Zr Sheet*
[From ref. 131]

Brazing alloy	Brazing cycle		Vacuum, torr		Remarks
	Temperature, °F	Hold, minutes	Cold	Hot	
83Ti-17Cu ^a	1830	12	5×10^{-5}	9×10^{-3}	Leaker; metal discolored.
83Ti-17Cu ^a	1850	15	3×10^{-6}	6×10^{-5}	Leaker; braze discolored.
83Ti-17Cu ^b	1980	30	3×10^{-6}	3×10^{-4}	Stress fracture of joint.
80Ti-20Ni.....	1925	20	7×10^{-7}	1×10^{-4}	Leaker; poor braze to ceramic.
80Ti-20Ni ^c	1925	15	1×10^{-6}	5×10^{-5}	Good braze fillets; backup ring cracked.
72Ti-28Cu ^{b, d}	1870	15	1×10^{-6}	3×10^{-5}	Columbium alloy cracked.
72Ti-28Cu ^{b, d, e}	1870	7	5×10^{-6}	4×10^{-5}	Good fillets but porous braze.

^aCopper washer to form brazing alloy was adjacent to ceramic.

^bCopper washer to form brazing alloy was adjacent to columbium alloy.

^cThe ceramics were coated with lithium molybdate to improve reaction.

^dAn excess of copper was used to compensate for its evaporation.

^eA 9-hour hold at 1200° F during cooling to relax residual stresses.

cent beryllia ceramic was exposed in potassium or lithium vapor at 1000° F for 500 hours. Niobium-base alloy Nb-1Zr was selected as the metal member in ceramic-to-metal joints; some joints were also made with D43 (Nb-10W-1Zr-0.1C).

2. *Brazing with metallized ceramic surfaces.*—The effectiveness of tungsten-base metallizing paints in promoting strong, leaktight ceramic-to-metal joints was investigated. The metallizing paints contained 85 to 95 percent tungsten and 5 to 15 percent rare earth oxides, alumina, and/or calcium carbonate. Joints were made using ASTM test specimens made from ceramics containing 99.0 percent alumina, 99.7 percent alumina, and 99.8 percent beryllia. The results of the joining studies with alumina ceramics are shown in table 19; acceptable strength levels

were obtained but problems were encountered with brazing-alloy metallized-coating reactions and cracking in the joint. The tests with metallized beryllia ceramics did not produce acceptable results because the joint strength was too low for the intended application. The studies with metallized ceramic surfaces were discontinued in favor of active metal brazing.

3. *Active metal brazing.*—The use of active metals in brazing ceramic-to-metal joints for service in alkali metal vapors at elevated temperatures was studied extensively. Promising active metal brazing alloys were selected using ASTM test specimens and modulus-of-rupture test bars (table 20). On the basis of these tests the following alloys were selected for further evaluation: 75Zr-19Nb-6Be, 56Zr-28V-16Ti, and 48Ti-48Zr-4Be. Vacuum leak test speci-

TABLE 19.—*Tensile Strength and Leak Testing of Special Metallizing Paints Utilizing ASTM CLM 15 Tensile Test Assembly*

[From ref. 137]

Paint symbol	Copper braze ^a							Nickel alloy braze ^b		
	Ei3-3W (99.7 percent Al ₂ O ₃)				AD 99 (99 percent Al ₂ O ₃)			AD 99 (99 percent Al ₂ O ₃)		
	Number of tests	Tensile strength, psi	Number of tests	Leak test	Number of tests	Tensile strength, psi	Number of tests	Leak test	Number of tests	Leak test
W5M	1	>14 850	2	VT						
W8M	1	>12 900	2	VT						
W9M	1	>14 550	2	VT						
W10M	1	>13 200	2	VT						
W11M	1	>14 400	1	VT	2	>12 600	2	VT	1	LKR
W12M	1	^c 6030	1	LKR	2	>11 250	2	VT	1	VT
W13M	1	>12 900	1	VT	2	>11 160	2	VT	1	VT
W14M	1	^c 8160	1	VT	2	>13 110	2	VT	1	LKR
W15M	1	^c 4050	1	VT	2	>13 290	2	VT	1	LKR

^a Copper brazed in -100° F dewpoint hydrogen at 2040° F with 3-minute hold at temperature. 0.020-inch 70/30 cupro-nickel washer between CLM 15 pieces.

^b Coast Metals Braze Alloy 52 (3B, 4.5Si, 0.15C, Ni balance) brazed at 1850° F in vacuum at 10⁻⁵ torr with no hold time at temperature. 0.015-inch Columbium washer between CLM 15 pieces. Columbium washer and metallizing plated with 0.0005 inch Fe; vacuum-sintered for 10 minutes at 1470° F.

^c Specimens broke in the AD 94 side of the joint.

NOTES:

(1) > indicates a metallizing strength greater than the figure shown. The specimen broke in the ceramic at the stress level noted.

(2) VT indicates a leak rate less than 1×10⁻⁹ torr-liters/sec as determined in leak-testing procedure.

(3) LKR indicates leaker.

(4) All paints listed were sintered for ½ hour at 3045° F in forming gas, 75N₂-25H₂, 70° F dewpoint.

TABLE 20.—*Active Braze Alloy Preliminary Screening Using Cb-1Zr Metal Member with Designated Ceramic*

[From ref. 137]

Braze composition, weight percent	Brazing Temperature, ° F	Thermalox 998 99.8% BeO		Ei3-3W Al ₂ O ₃		Remarks
		VT ^b	Strength (MoR) ^a , psi	VT ^b	Tensile Strength ^a , psi	
75Zr-19Cb-6Be-----	1940	2/4	15 260	4/4	9750	Wets columbium alloy D-43 well.
68Ti-28V-4Be-----	2370	1/4	16 635	1/4 0/4	>240 >4475*	Wets columbium alloy D-43 and tantalum alloy T111 well.
56Zr-28V-16Ti-----	2270	°	15 740	2/4	4850	Wets columbium alloy D-43 well.
48Ti-48Zr-4Be-----	1940	3/4	16 500	4/4	4900	
46Ti-46Zr-4V-4Be---	1830	-----	16 650	4/4	9575*	
50Zr-30V-20Cb-----	2415	3/4	15 175	1/4 0/4	6938* 140	
65V-35Cb-----	3400	-----	-----	-----	-----	No test.
70Ti-30V-----	3000	-----	-----	-----	-----	No test.
60Zr-25V-15Cb-----	2435	-----	14 035	0/4	50	Forms skull on columbium alloy D-43 and tantalum alloy T111.
50Zr-30Ti-20V-----	2480	0/4	>4 742	0/4	>202	Forms skull on columbium alloy D-43 and tantalum alloy T111, Cb-1Zr alloy.
40Zr-30Ti-30V-----	2335	4/4	13 165	0/4	245	Wets columbium alloy D-43 and tantalum alloy T111 well.
35Ti-35V-30Zr-----	2595	0/4	>10 280	0/4	>500	No test. Wets columbium alloy D-43 and tantalum alloy T111 well.
50Ti-30Zr-20V-----	2595	-----	-----	-----	-----	
62Ti-30V-8Si-----	2480	4/4	8 370	0/4	>1175	

^a Modulus of rupture.^b Number vacuum tight over total number tested.

° Vacuum-tight assemblies fabricated previously on another program (SPUR, Westinghouse).

NOTES:

(1) Brazed in vacuum furnace (10⁻⁵ torr) at temperature indicated; no hold time. Results shown are from the best braze run for each alloy.(2) *Made with AD 99 alumina + 99 percent Al₂O₃.

(3) >Indicates incomplete melting—greater strengths might be expected with increased temperature but were not attempted because of excessive pressure in the furnace at elevated temperature.

(4) Italicized brazes and ceramic-to-metal assemblies were considered most favorable for further evaluation in potassium, potassium-sodium eutectic, and lithium.

mens, modulus-of-rupture test specimens, and tab peel assemblies of high-purity alumina and beryllia were vacuum-brazed to Nb-1Zr or D43 alloy metal members with these three alloys. The ceramic-to-metal joints were tested in the as-

brazed condition, after exposure in vacuum for 500 hours at either 1000° or 1600° F, and after exposure in alkali metal vapors for 500 hours at either 1000° or 1600° F. The results are summarized in tables 21 and 22. Metallographic

TABLE 21.—*Effect of 500 Hour 1600° F Potassium Vapor Exposure on the Room Temperature Flexural Strength of Selected Ceramic-Metal Sealing Systems*

[From ref. 137]

Ceramic	Braze, weight percent	Brazing temperature, ° F	Key	Flexural strength, psi		
				As brazed	Vacuum exposed 500 hr, 1600° F	Potassium vapor 500 hr, 1600° F
Ei3-3W alumina, 99.7 percent Al ₂ O ₃ ----	75Zr-19Cb-6Be	1940	\bar{x}	25 655	12 965	^a 0
			<i>s</i>	7 370	^b 4505	
			<i>n</i>	11	2	4
Ei3-3W alumina, 99.7 percent Al ₂ O ₃ ----	48Ti-48Zr-4Be	1940	\bar{x}	23 342	19 760	^a 0
			<i>s</i>	4 690	^b 1440	
			<i>n</i>	12	2	4
Thermalox 998, beryllia 99.8 percent BeO.	75Zr-19Cb-6Be	1940	\bar{x}	15 404	17 300	^c < 1000
			<i>s</i>	1 220	^b 800	
			<i>n</i>	5	2	5
Thermalox 998, beryllia 99.8 percent BeO.	48Ti-48Zr-4Be	1940	\bar{x}	16 559	14 250	^c 10 538
			<i>s</i>	2 500	-----	3740
			<i>n</i>	8	1	5
Thermalox 998, beryllia 99.8 percent BeO.	56Zr-28V-16Ti	2270	\bar{x}	13 503	13 985	^c 11 810
			<i>s</i>	2 870	^b 1715	850
			<i>n</i>	6	2	5

^a No MoR structures survived exposure test intact.^b Standard deviation has little significance for sample size of two pieces.^c Accompanying vacuum leak test assemblies were broken during removal from capsule.

NOTES:

(1) All tests on modulus-of-rupture assemblies (MoR) using columbium-1 percent Zr metal member.

(2) Italicized ceramic-metal sealing systems appear to be the best of those tested.

KEY:

 \bar{x} —arithmetic mean.*s*—standard deviation.*n*—number of specimens tested.

examinations of the ceramic-to-metal joints were also made, and all studies were analyzed to select the best ceramic-to-metal seal system for each alkali metal-temperature environment (table 23).

4. Wetting was enhanced by depositing thin layers of titanium and molybdenum on ceramic surfaces by evaporation techniques.

The work on active metal brazing of ceramic-to-metal joints for service in alkali metal vapors at high temperatures has been continued at Westinghouse under a followup program. In a recent quarterly report, Kueser indicated that additional brazing studies had been conducted to select other alloys for joining a 99.8-percent beryllia ceramic to an Nb-1Zr alloy metal mem-

ber for service in potassium vapor at temperatures up to 1600° F. (ref. 138). The results of these studies are summarized in table 24. The following three alloys were selected for further evaluation: 46Ti-46Zr-4Be-4V, 60Zr-25V-15 Cb, and 35 Ti-35Zr. A topical summary report on this program is expected to be published later in 1968. It has been reported that a 4-inch-diameter BeO bore seal has been operated for 6000 hours in potassium metal vapor at 1300° F.

The active metal process has been investigated in a number of programs as a means to fabricate ceramic-to-metal seals and composite structures for use in cesium-plasma thermionic converters. In addition to producing joints be-

TABLE 22.—*Effect of 500-Hour 1000° F Potassium, NaK, or Lithium Vapor Exposure on the Room Temperature Flexural Strength of Selected Ceramic-Metal Sealing Systems*

[From ref. 137]

Ceramic	Metal member	Braze alloy, weight percent	Brazing temperature, °F	Alkali metal	Key	Room temperature flexural strength, psi			Alkali metal exposed leak test ^a	Remarks room temperature flexural strength and leak tests
						As brazed	Vacuum exposed 500 hr, 1000° F	Alkali metal exposed 500 hr, 1000° F		
Thermalox 998, beryllia 99.8 percent BeO.	Columbium D-43	75Zr-19Cb-6Be	1940	K ^a	\bar{x} s	14 343 3740	14 450 250	14 340 490	2/2 VT	Very good results.
Thermalox 998, beryllia 99.8 percent BeO.	Columbium D-43	48Ti-48Zr-4Be	1940	K ^a	\bar{x} s	7 14 130 4090	2 Not tested	2 9710 1940	2/2 VT	Fair results.
Thermalox 998, beryllia 99.8 percent BeO.	Cb-1Zr	56Zr-28V-16Ti	2270	Li ^c	\bar{x} s	13 503 2870	12 895 555	12 000	4/4 VT	Good results.
Ei3-3W, alumina 99.7 Al ₂ O ₃ .	Cb-1Zr	75Zr-19Cb-6Be	1940	K ^a	\bar{x} s	25 655 7370	21 100 3300	21 432 2250	3/3 VT	Good results.
Ei3-3W, alumina 99.7 percent Al ₂ O ₃ .	Cb-1Zr	48Ti-48Zr-4Be	1940	K ^a	\bar{x} s	11 23 342 4690	2 16 335 2140	3 6120 3500	4/4 VT	Fair results.
Ei3-3W, alumina 99.7 percent Al ₂ O ₃ .	Cb-1Zr	75Zr-19Cb-6Be	1940	NaK ^b	\bar{x} s	25 655 7370	22 100 3300	9587 1320	4/4 VT	Fair results.
Ei3-3W, alumina 99.7 percent Al ₂ O ₃ .	Cb-1Zr	48Ti-48Zr-4Be	1940	NaK ^b	\bar{x} s	11 23 342 4690	2 16 335 2140	4 10 390 1820	4/4 VT	Fair results.

^aOxygen level in associated purity test capsule was less than 10 ppm.

^bOxygen levels in two associated purity test capsules were less than 10 ppm.

^cAssociated purity test capsule leaked; no meaningful determination.

^dStandard deviation has little significance for a sample size of two pieces.

^eVT indicates helium leak rate of less than 1×10^{-9} torr-liter/second.

^fOne sample only.

NOTE: All tests on modulus-of-rupture assemblies (MoR) using column-1 percent zirconium metal member.

Key:

\bar{x} —arithmetic mean.

s—standard deviation.

n—number of specimens tested.

TABLE 23.—*Best Ceramic-to-Metal Sealing System Tested in Each Alkali Metal-Temperature Environment*

[From ref. 137]

Environment	Ceramic	Brazing alloy	Average room temperature flexural strength, ^b psi
Potassium 1600° F-----	Thermalox 998, beryllia 99.8 percent BeO.	56Zr-28V-16Ti	11 810
Potassium 1000° F-----	Ei3-3W, alumina 99.7 percent Al ₂ O ₃ .	75Zr-19Cb-6Be	21 432
NaK 1000° F ^a -----	Ei3-3W, alumina 99.7 percent Al ₂ O ₃ .	48Zr-48Ti-4Be	10 390
Lithium 1000° F-----	Thermalox 998, beryllia 99.8 percent BeO.	56Zr-28V-16Ti	>12 000

^a Marginal usefulness after 500 hours.

^b Postexposure flexural strength.

NOTE: All seal systems were made with 0.015-inch-thick columbium-1 percent zirconium alloy metal member.

tween metals and metallized ceramic bodies, engineers at the Los Alamos Scientific Laboratory used active metal alloys to braze unmetallized high-alumina ceramics to Nb-1Zr (ref. 131). Using the joint design shown earlier in figure 17(c), seals were made in a cold-wall resistance furnace at 10^{-4} torr with 58V-32Nb-10Ti, 57Ti-19Nb-12V-9.5Cr-2.5Al, and 99.5Zr-0.5Ni. The results of these tests are shown in table 25. Research to join alumina to Nb-1Zr, conducted for the Los Alamos Scientific Laboratory by the Pyromet Company, has been reviewed by Kirby and LaMotte (ref. 132). Several filler metals were evaluated for joining metallized and unmetallized alumina sleeves to an Nb-1Zr base section; subsequently, research was concentrated on 62Ti-4Zr-8Mo-26Fe and 48Ti-48Zr-4Be as filler metals for joining uncoated alumina (Al_2O_3 -0.5Y₂O₃) to Nb-1Zr. The joint design was similar to that shown in figure 17(c). The results of the brazing tests are shown in table 26. In 1962, Bristow (General Electric Company) reported on an extensive investigation of the active metal process to fabricate ceramic-to-ceramic and ceramic-to-metal joints for service in a cesium vapor environment up to about 900° C (1652°F) (ref. 139). All joints were made with titanium-nickel

filler metals. To make ceramic-to-ceramic joints, two ceramic cylinders (0.690 inch O.D., 0.480 I.D., and 0.200 inch long) were brazed together; joints were made by brazing two of the ceramic cylinders to either side of a 0.010-inch-thick metal washer. Of the two ceramics used during these studies, one was a silica-free, high-purity alumina body suitable for a cesium vapor environment and the other a 97-percent alumina ceramic containing 3 percent CaO, MgO, and SiO₂ as fluxing oxides. The metals studied included titanium, nickel, tantalum, Kovar, and Types 304 and 430 stainless steel. Nickel and titanium shim stock of various thicknesses was used as the filler metal. The alloy composition was controlled by stacking up nickel and titanium washers of different thicknesses and placing them in the joint area. For example, an alloy with the composition 71.8Ti-28.2Ni was produced by stacking a washer of 0.001-inch-thick titanium between two washers of 0.0003-inch-thick nickel; the composition of this filler metal is very similar to that of the nickel-titanium eutectic, 71.5Ti-28.5Ni. This investigation emphasized the microstructures that form during brazing, their properties, their behavior in high-temperature environments, and the means that can be used to alter their com-

TABLE 24.—Summary of Brazing Data for Selecting Brazing Alloys to Join Thermalox 998 Beryllia Ceramic to Columbium-1 Percent Zirconium Metal

[From ref. 138]

Brazing alloy number	Nominal alloy composition, weight percent	Brazing conditions		Strength of brazed specimens						Leak test *		
				Modulus of rupture			Tab peel strength					
		Time, min-utes	Tem-pera-ture, ° F	Num-ber of speci-mens	Re-marks	Average strength, psi	Standard deviation, ^d psi	Num-ber of speci-mens	Re-marks		Average strength, pounds/inch	Standard deviation, ^d pounds/inch
2	68Ti-28V-4Be	5	2372	14	(a)	17 465	1900	6	(c)	9	2	6/8 VT
5	46Ti-46Zr-4Be-4V	5	1832	17	(a)	16 800	3220	8	(c)	19	17	5/6 VT
6	50Zr-30V-20Cb	5	2516	6	(a)	15 150	2160	4	(b)	21	3	2/2 VT
9	60Zr-25V-15Cb	5	2436	12	(a)	15 000	875	6	(b)	34	9	6/6 VT
10	50Zr-30Ti-20V	10	2732	4	(b)	15 225	3140	2	(b)	21	<i>s</i> ± 1	0/2 VT
12	35Ti-35V-30Zr	1	2804	3	(a)	24 433	1380	2	(c)	16	<i>s</i> ± 0	2/2 VT

* Good wetting, good fillet.

* Fair wetting, incomplete fillet.

* Poor wetting, incomplete, granular fillet.

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}}$$

* VT indicates a leak rate $< 1 \times 10^{-9}$ std. cc/sec., 2/3 indicates 2 of 3 samples vacuum tight, etc.

* When there were less than three specimens, the standard deviation was not determined; the value shown indicates the spread of values from the average value.

NOTE: Ceramic parts were Brush Beryllia's 99.8 percent BeO body containing 70 ppm SiO₂ (Lot No. 1) or 150 ppm SiO₂ (Lot No. 2). The parts were fabricated by dry-pressing slabs, firing in electric kiln, and subsequent cutting and grinding to shape. The ceramic bar size was 0.1 by 0.1 by 1 inch. Density was between 2.85 and 2.94 g/cc, as specified by vendor. Average postbrazing modulus-of-rupture strength of the ceramic was 25 000 psi. Ten bars from above assemblies were tested. The standard deviation was 3230 psi. The metal member was 0.015-inch-thick Ob-1 percent Zr sheet.

TABLE 25.—*Evaluation of Brazing Alloys With Unmetallized Alumina Ceramics*

[From ref. 131]

Brazing alloy composition, w/o	Ceramic type ^a	Brazing temp., ° C	Remarks
V-32Co-10Ti	Al-300-----	1800	Good wetting of ceramic and metal. Limited alloying with metal (0.003 in.) and limited intergranular attack of ceramic.
V-32Co-10Ti	Lucalox-----	1800	Fair wetting of ceramic, good wetting of metal.
Ti-19Cb-12V-9.5Cr-2.5Al.	Al-14-----	1700	Good wetting of metal, extensive intergranular attack of ceramic.
Ti-19Cb-12V-9.5Cr-2.5Al.	Lucalox-----	1700	Good wetting of metal, fair wetting of ceramic.
Zr-0.5Ni	Al-14 and lucalox-----	1830	Good wetting of metal, but severe attack of the ceramics.
Co	Al-14-----	1540	Extreme alloying with the metal. Good wetting of metallized ceramic.

^a	Ceramic type	Density, percent theo	Composition
Al-300-----		95	97.6 w/o Al ₂ O ₃
Al-14 (pressed)-----		93	Al ₂ O ₃ -0.5 w/o Y ₂ O ₃
Al-14 (slipcast)-----		96	Al ₂ O ₃ -0.5 w/o Y ₂ O ₃
Lucalox-----		98	Al ₂ O ₃ -0.3 w/o MgO

TABLE 26.—*Evaluation of Active Metal Brazing Alloys With Unmetallized Alumina (Al₂O₃-0.5Y₂O₃)*

[From ref. 132]

Spec. number	Filler alloy	Method of placement	Brazing temperature		Holding time, min	Results	
			° F	° C		Visual	Leak test
1	Ti-4 Zr-8 Mo-26 Fe	Organic binder.	2280-----	1249	5	Fillet 90 percent complete.	Gross leak.
2	Ti-4 Zr-8 Mo-26 Fe	Organic binder.	2440-----	1338	None	Fillet 50 percent complete.	Gross leak.
3	Ti-4 Zr-8 Mo-26 Fe	Organic binder.	2300-----	1260	1	Fillet 50 percent complete.	Gross leak.
4	Ti-4 Zr-8 Mo-26 Fe	Organic binder.	2290-----	1254	5	Fillet 100 percent complete.	Gross leak.
5	Ti-4 Zr-8 Mo-26 Fe	Organic binder.	2280-----	1249	5	Fillet 100 percent complete.	Gross leak.
6	Ti-4 Zr-8 Mo-26 Fe	Organic binder.	2280-----	1249	5	Fillet 100 percent complete.	Gross leak.
			Rebrazed at 2290.	1254	2	Fillet 100 percent complete.	Gross leak.
7	Ti-48 Zr-4 Be	Organic binder.	2000-----	1093	5	No fillet-----	Gross leak.
8	Ti-48 Zr-4 Be	Organic binder.	1970-----	1077	5	No fillet-----	Gross leak.
			Rebrazed at 2000.	1093	5	Fillet 90 percent complete.	Leaktight.

TABLE 26.—*Evaluation of Active Metal Brazing Alloys With Unmetallized Alumina ($Al_2O_3-0.5Y_2O_3$)—*
Continued

Spec. number	Filler alloy	Method of placement	Brazing temperature		Holding time, min	Results	
			° F	° C		Visual	Leak test
9	Ti-48 Zr-4 Be	Organic binder.	1970.....	1079	7	No fillet.....	Gross leak.
			Rebrazed at 2350.	1288	5	Fillet 90 percent complete.	Leaked at 5×10^{-5} cc/sec.
10	Ti-4 Zr-8 Mo-26Fe	Organic binder.	1950.....	1065	5	Fillet 70 percent complete.	Gross leak.
11	Ti-48 Zr-4 Be	Organic binder.	2140.....	1171	5	Fillet 50 percent complete.	Leaked at 1×10^{-7} cc/sec.
			Rebrazed at 2350.	1288	5	Fillet 50 percent complete.	Leaked at 1×10^{-7} cc/sec.
12	Ti-48 Zr-4 Be	Zr foil ledge.	1950.....	1065	5	Fillet 80 percent complete.	Gross leak.
13	Ti-48 Zr-4 Be	Zr foil ledge.	2100.....	1149	None	Fillet 60 percent complete.	Leaked at 1×10^{-9} cc/sec.
14	Ti-4 Zr-8 Mo-26 Fe	Zr foil ledge.	2290.....	1254	15	Fillet 80 percent complete.	Leaked at 1×10^{-8} cc/sec.
15	Ti-48 Zr-4 Be	Zr foil ledge.	2300.....	1260	None	Fillet 50 percent complete.	Ceramic cracked.
16	Ti-48 Zr-4 Be	Zr foil ledge.	2100.....	1149	15	Fillet 30 percent complete.	Leaked at 5×10^{-7} cc/sec.

position. A brittle intermetallic compound Ti_2Ni forms when the eutectic composition is exceeded toward the nickel-rich side of the nickel-titanium phase diagram. Wisser and Hagadorn have studied nickel-titanium microstructures in brazed ceramic-to-ceramic joints and noted the presence of small cracks in an alloy containing 32.1 percent nickel and large cracks in an alloy containing 35 percent nickel (ref. 140). On the basis of these studies, Bristow concluded that:

1. Seals or sealing alloys containing a titanium phase in contact with alumina were unsuitable for long-time service at 700° C (1292° F) or for short-time service at 900° C (1652° F) because the active metal alloy continued to re-

act with the ceramic at the service temperature and became embrittled.

2. Seals to thick titanium members minimized the formation of Ti_2Ni .

3. The ceramic composition had no apparent effect on the reaction rate between the ceramic and an alloy containing a titanium phase at 900° C (1652° F). At 700° C (1292° F), the reaction rate appeared lower with the high-purity alumina ceramic than with the ceramic containing a glassy phase.

4. Service lives up to 2000 hours were recorded at 700° C (1292° F) for alumina-to-titanium and alumina-to-tantalum seals.

5. At 900° C (1652° F), the only seals that had lives exceeding a few hundred hours were

alumina-to-nickel joints made with titanium shim stock under conditions that precluded the formation of α -titanium or Ti_2N .

During further research on the active metal process, conducted by Bristow, Grossman, and Kaznoff (ref. 11), seals were made between a high-purity alumina body and nickel, molybdenum, tantalum, and niobium. The alumina-

to-niobium seals exhibited the best high-temperature properties, being vacuum-tight after 2000 hours exposure at 900°C (1652°F) and after 240 hours exposure at 1075°C (1967°F). The alumina-to-molybdenum joints also had good high-temperature behavior; however, poor properties were observed with the alumina-to-nickel and alumina-to-tantalum joints.

Joining Graphite

PROPERTIES AND USES OF GRAPHITE

The industrial uses of graphite seem almost limitless. Because of its high melting (sublimation) temperature and resistance to thermal shock, much of the graphite produced in the United States is used for electrodes in electric steel-making furnaces and for anodes in electrolytic processing equipment. Graphite is also used for anodes in high-power electronic tubes, for brushes in rotating electrical machinery, as a mold material for casting, as a refractory for lining furnaces, and as a constituent in powder metallurgy products. These applications require little or no graphite-to-metal joining.

Graphite also has become exceedingly important, however, in nuclear and aerospace applications that require graphite to be joined to itself and metallic components. Because of its low absorption cross section for fast neutrons, graphite is used in nuclear reactors as a material for moderators, reflectors, and thermal columns. Also, composites of graphite and materials with high neutron cross sections can be used for control rods and shielding.

Because graphite has exceptional resistance to thermal shock and a favorable strength-to-weight ratio at high temperatures, it is used widely as a nozzle material for solid-fuel rocket engines. The rocket exhaust environment is characterized by temperatures of 600° F (315° C) or higher, supersonic gas flow, reactive and abrasive combustion products, and steep temperature gradients. For such an application, the ideal structural material should have the following properties: low specific weight; high

melting temperature; good thermal conductivity; superior resistance to thermal shock; resistance to oxidation, corrosion, and erosion; and adequate strength and ductility over the service temperature range. While graphite does not satisfy all of these requirements, it does possess many of the desired properties. For some rocket nozzle applications, the graphite nozzle is backed up by a metal liner. If the firing time is long enough to cause erosion of the graphite, a tungsten nozzle backed up by a graphite liner is used. In either case, a sound graphite-to-metal joint is required to obtain the desired performance. Graphite has also been used in the fabrication of jet vanes for controlling the yaw and pitch attitudes of rockets.

Selected properties of graphite are shown in table 27; the properties of metals used for high-temperature service are included for comparison (refs. 29 and 46). Not only do the physical and mechanical properties of graphite vary widely in accordance with the method used to produce the graphite and the type and purity of the starting materials, but the requirements of industry vary also. For example, nuclear reactor grade graphite used as a moderator must have a high degree of purity, because impure elements affect the magnitude of the absorption cross section. The mechanical properties of graphite are here of secondary importance, but they are of primary importance when graphite is used as a structural material in the production of aerospace hardware.

Significant progress in producing graphite with consistent properties has been made in response to the requirements of the aerospace and

TABLE 27.—Selected Properties of Some Structural Materials

[From refs. 29 and 46]

Metal	Density, g/cc at 20° C	Melting point, °C	Thermal conductivity, cal/cm·°C/cm	Coefficient of linear thermal expansion, cm/cm·°C × 10 ⁻⁷	Vapor pressure, torr 1.316 × 10 ⁻³ atm	Young's modulus 20° C, psi
Nickel.....	8.90	1453	0.198/100° C 0.175/200° C 0.152/300° C 0.142/400° C 0.148/500° C	133.0/25 to 100° C 144.0/25 to 300° C 155.0/25 to 600° C 163.0/25 to 900° C	10 ⁻⁹ /912° C 10 ⁻⁴ /1247° C 10 ⁻² /1497° C 10 ⁻¹ /1667° C	30 × 10 ⁶ .
Iron.....	7.87	1537	0.163/100° C 0.147/200° C 0.081/800° C	121.0/20 to 100° C 134.0/20 to 300° C 147.0/20 to 600° C 150.0/20 to 900° C	10 ⁻⁸ /877° C 10 ⁻⁴ /1207° C 10 ⁻² /1467° C 10 ⁻¹ /1637° C	28.5 × 10 ⁶ .
Columbium.....	8.57	2468 ± 10	0.125/0° C 0.135/200° C 0.145/400° C 0.156/600° C	73.9/0 to 400° C 75.6/0 to 600° C 77.2/0 to 800° C 78.8/0 to 1000° C	2.00 × 10 ⁻⁴ /2031° C 1.85 × 10 ⁻⁴ /2323° C	12.4 × 10 ⁶ .
Molybdenum.....	10.22	2620 ± 10	0.298/204° C 0.289/427° C 0.272/649° C 0.254/871° C 0.215/1649° C 0.206/2204° C	54.3/20 to 149° C 51.9/20 to 482° C 53.6/20 to 649° C 58.0/20 to 982° C 62.8/20 to 1316° C 66.5/20 to 1593° C	10 ⁻³ /1582° C 10 ⁻⁴ /2167° C 10 ⁻² /2627° C 10 ⁻¹ /2927° C 1/3297° C	47 × 10 ⁶ .
Tantalum.....	16.6	2996	0.130/20° C 0.162/568° C 0.171/828° C 0.179/1106° C 0.188/1416° C	65.0/0 to 1000° C 66.0/20 to 500° C 73.0/27 to 1400° C 78.0/27 to 2400° C	10 ⁻³ /1957° C 10 ⁻⁴ /2587° C 10 ⁻² /3067° C 10 ⁻¹ /3372° C	27 × 10 ⁶ .
Tungsten.....	19.3	3395 ± 15	0.31/20° C 0.275/927° C 0.268/1127° C 0.260/1327° C 0.253/1527° C 0.245/1727° C	44.4/27° C 51.9/1027° C 72.6/2027° C	10 ⁻⁸ /2077° C 10 ⁻⁴ /2957° C 10 ⁻² /3297° C 10 ⁻¹ /3642° C	50 × 10 ⁶ .
Graphite.....	1.7	3652 to 3697	0.02 to 0.5/20° C	10.0 to 50.0/20° C (varies widely).	10 ⁻⁸ /1950° C 10 ⁻⁴ /2380° C 10 ⁻² /2700° C 10 ⁻¹ /2900° C 10 ⁰ /3140° C 10 ² /3800° C	0.8 to 1.4 × 10 ⁶ (varies widely).

nuclear industries. Among the most important advances is the development of pyrolytic graphite, which consists of highly oriented planes of graphite molecules closely stacked in a laminated structure as shown in figure 18 (ref. 140). The bonding forces between atoms in a given plane (a and b direction) are much stronger than the bonding forces between planes. As a result, the properties of pyrolytic graphite are highly directional as shown in table 28 and figure 19. These differences in properties must be considered in designing a structure that incorporates graphite; similarly, the dependence of properties on the crystal orientation of graph-

ite has a profound effect on the design of a graphite-to-metal joint.

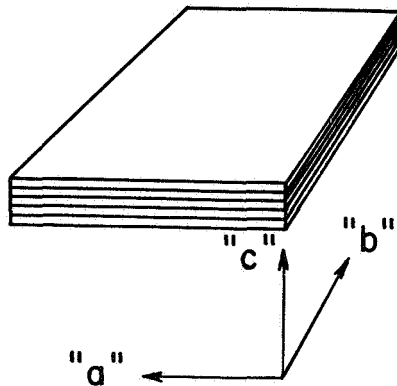


FIGURE 18.—Schematic representation of pyrolytic graphite structure (ref. 140)

TABLE 28.—Typical Room-Temperature Properties of Pyrolytic Graphite

[From ref. 141]

	Pyrolytic graphite	
	a or b direction	c direction
Tensile strength, psi.....	15 000	750
Young's modulus, psi $\times 10^6$..	4	
Thermal conductivity (1000° F), Btu-ft/ft ² sec F $\times 10^4$ ---	280 to 370	0.8 to 2.9
Specific heat.....	0.18	0.18
Specific gravity.....	2.21	2.21

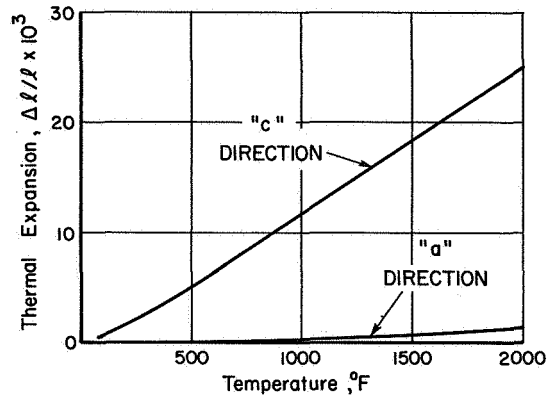


FIGURE 19.—Thermal expansion characteristics of pyrolytic graphite (ref. 140)

JOINING CONSIDERATIONS

Graphite-to-metal joints are difficult to design and produce because graphite is not wet readily by most conventional filler metals, the physical and mechanical properties of graphite differ significantly from those of most structural metals, and only a few processes can be used for joining. The problems of joining graphite are very similar to those of joining ceramics to other materials, and the same care must be observed in selecting the filler metal, joining process, and joint design.

Most filler metals do not wet graphite well and do not exhibit their usual excellent flow properties. Filler metals used to join graphite to graphite or graphite to metals should contain constituents that have a strong tendency to form carbides, since the bonding mechanism depends on carbide formation. Thus, filler metals containing substantial amounts of titanium, zirconium, chromium, silicon, or niobium are most successful; however, they are not commercially available, although several experimental alloys have been patented.

The differences between the linear thermal-expansion coefficients of graphite, the filler metal, and the base metal cause the difficulty in designing and producing graphite-to-metal joints; graphite, in comparison with metallic elements, has a small expansion coefficient. The

graphite and metal workpieces expand and contract at different rates during the heating and cooling portions of the joining cycle; as a result, stresses that can cause cracking are established in the joint area. Graphite-to-metal joints must be carefully designed to minimize such stresses. Because of graphite's low tensile strength, the joint should be designed so that the graphite workpiece is compressed. Particular care must be observed when joining pyrolytic graphite, because the expansion coefficient varies widely as a function of crystal orientation.

FUSION JOINING OF GRAPHITE

The methods that can be used to join graphite to itself and to metals are limited to the non-fusion joining techniques, i.e., solid-phase joining and liquid-solid-phase joining. Most research has been concentrated on the diffusion welding and brazing processes. Kareta and Nefedov reported on experimental studies to arc-weld graphite-to-graphite joints (ref. 142). The joints were produced with a straight-polarity, direct-current arc; a consumable graphite electrode was used as the filler metal. Although a joint was produced, its strength was too low for practical use. No reports on arc-welding graphite to metal were found.

NONFUSION JOINING OF GRAPHITE

Solid-Phase Joining

Only limited research has been conducted on the solid-phase or diffusion welding of graphite to itself or to metals, because satisfactory joints cannot be produced without a diffusion aid. Kareta and Nefedov reported that anode-grade, electrode-grade, and pyrolytic graphite plates were diffusion-welded in an inert atmosphere using titanium, zirconium, niobium, tantalum, or hafnium foil inserts between the graphite workpieces (ref. 142). The joining conditions were as follows: temperature 2300° to 3000° C (4172° to 5432° F); pressure 1422 psi; and time 3 to 6 minutes. The tensile strength of joints made with a 0.004-inch-thick zirconium insert varied from 2247 psi for anode- and electrode-grade graphite to 7082 psi for pyrolytic graphite in the a or b direction.

According to a British patent, graphite has been diffusion-welded to mild steel in a pure carbon dioxide atmosphere (ref. 143). The workpieces were bonded at 4480 psi for 200 hours; the bonding temperature was not given.

Solid-phase joining was investigated in a program directed toward joining tungsten to graphite for aerospace applications at temperatures up to 5000° F (2760° C) (ref. 144). Various materials were used to promote diffusion. This research is summarized below:

1. For joining graphite to tungsten in a vacuum at 3600° F (1982° C), the joint interface was coated with a mixture of molybdenum, carbon, and ruthenium powders to promote bonding; however, little or no bonding occurred.

2. A titanium-carbide layer was produced on a graphite substrate by coating the substrate with titanium hydride and firing the specimen at 4700° F (2593° C). A similar procedure was used to produce a titanium coating on the tungsten substrate. Then, the coated surfaces were butted together and the assembly diffusion-welded at 4700° F (2593° C) in a vacuum. Joining did not occur. Attempts to join graphite coated with titanium carbide to tungsten coated with colloidal graphite were also unsuccessful.

3. The use of a titanium foil insert between the graphite and tungsten surfaces was also unsuccessful. The solid-phase joining approach was eliminated during this program, because a technique involving the formation of a liquid phase during bonding appeared more successful. (This work will be discussed in the next section.)

Bondarev reported that a variation of diffusion-welding—eutectic-diffusion welding—produced sound joints between graphite and several refractory metals (ref. 145). A titanium foil insert, 0.004 inch thick, was electroplated with a 0.0008- to 0.001-inch-thick layer of copper and placed between the workpieces. Joints between graphite and molybdenum, niobium, or tantalum were produced in a vacuum diffusion-welding unit under the following conditions: temperature 890° to 1050° C (1634° to 1922° F); pressure 43 to 100 psi; time 5 to 10 minutes. An eutectic occurs in the Ti-Cu system at 885° C (1607° F) where the weight percent of copper is 72. Under the welding conditions cited above,

the Ti-Cu eutectic alloy formed and wet the graphite and the refractory metal. The maximum joint strength occurred when the welding temperature was between 960° and 980° C (1760° and 1786° F). The graphite-to-tantalum joint had the highest strength 1735 psi; the strengths of the graphite-to-molybdenum and graphite-to-niobium joints were slightly lower.

Eutectic-diffusion welding was also used to join graphite to Zircaloy-2 sheet stock, 0.035 inch thick, as a means of stabilizing advanced sodium graphite reactor (ASGR) moderator cans (ref. 146). After depositing a controlled amount of copper on the metal surface by plasma-arc spraying, the graphite and copper-coated Zircaloy-2 parts were held in intimate contact in a vacuum furnace and heated to a temperature somewhat higher than the temperature at which the zirconium-copper eutectic forms. The joining temperature of 1800° F (982° C) ensured rapid and complete formation of the Zr-Cu eutectic when using the recommended thickness of copper (0.001 inch).

Liquid-Solid-Phase Joining

Brazing, a liquid-solid-phase joining method, has proved to be the most suitable process for joining graphite to itself and metals. Most of the research on the development of filler metals and brazing procedures discussed in the following sections has been conducted by firms and Government agencies active in the nuclear and aerospace fields.

Graphite-to-Graphite Joining

Graphite-to-graphite joints using zirconium as a filler metal for nuclear applications have been investigated by Burnett and Marengo (ref. 147). Zirconium wets graphite well, but a layer of zirconium carbide is formed during brazing. At high operating temperatures, differential thermal expansion between the graphite and the carbide causes failure because of the brittleness of the zirconium carbide. Molybdenum disilicide has also been investigated for use in producing graphite-to-graphite joints (ref. 148). Little or no penetration of the graphite occurred, and thermal cycling tests indicated

suitability of these joints for some nuclear applications.

In another program Lindgren investigated the use of titanium, molybdenum, molybdenum disilicide, silicon, zirconium, and an experimental Ni-Cu-Mo alloy as filler metals for brazing graphite and caps to a graphite sleeve (ref. 149). The most satisfactory joints were produced with silicon or zirconium.

The Japanese Atomic Energy Research Institute has been active in developing methods to join graphite to graphite with a brazing filler metal containing (by weight percent) 30 to 50 Ni, 0 to 20 Ti, and Bal. Fe (refs. 150 and 151). This alloy, used also to produce graphite-to-metal joints, is based on Invar (Fe-36Ni), which has a small expansion coefficient comparable to that of graphite; titanium was added to improve the wetting properties of this alloy. Graphite-to-graphite joints have been evaluated by sustained high-temperature tests at 600° C (1112° F); the joints did not appear to be brittle.

Davidson and Ryde received a patent on a method to join graphite to itself or to metals (ref. 152). Nickel is deposited on the graphite surfaces when the graphite workpieces are heated to 200° to 500° C (392° to 932° F) in an atmosphere of nickel carbonyl; then, the parts are joined with conventional brazing alloys.

Several additional filler metals, developed primarily to braze graphite-to-metal joints but also used to produce graphite-to-graphite joints, are discussed in the section below.

Graphite-to-Metal Joining

The most extensive research on brazing graphite to itself and metals has been conducted by the Oak Ridge National Laboratory (ORNL) in connection with the molten salt reactor program for the last 7 or 8 years (refs. 12, 153, and 154). Initially, the wetting characteristics of selected commercial and experimental filler metals on graphite were determined; later, filler metals were developed that would wet graphite readily and be resistant to corrosion by molten fluoride salts. Commercial filler metals used to braze stainless steels and nickel-base alloys were screened early in the program.

Neither the nickel-base filler metals nor the nickel-gold eutectic alloy wet graphite; wetting was achieved with a titanium-cored silver-copper alloy that has been used on other occasions to braze graphite to metal. Two experimental filler metals—48Ti-48Zr-4Be and 49Ti-49Cu-2Be—also wet graphite well (ref. 12). Experimental alloys based on the nickel-gold alloy system were then prepared and evaluated. (This alloy system was selected because the nickel-gold eutectic, Au-18Ni, was ductile and very resistant to corrosion by molten salts.) Tantalum or molybdenum were added to the basic alloys; these metals are strong carbide formers and, unlike zirconium and titanium, possess the required corrosion resistance. Numerous ternary alloys in the nickel-gold-tantalum (Ni-Au-Ta) and nickel-gold-molybdenum (Ni-Au-Mo) alloy systems were prepared and evaluated by wetting tests conducted at 1300° C (2372° F). In the Ni-Au-Ta alloy system, 60Au-10Ni-30Ta proved to be most effective in brazing graphite-to-graphite and graphite-to-molybdenum joints; however, this alloy had limited ductility and displayed fillet cracking. Filler metals that contained less tantalum were suitable for brazing graphite-to-molybdenum but not graphite-to-graphite joints. More promising filler metals were discovered in the Ni-Au-Mo alloy system. The 35Au-35Ni-30Mo alloy wet graphite readily and possessed excellent flow properties; it could be used to join graphite to itself or to molybdenum. Similar alloys containing lower concentrations of molybdenum were quite suitable for joining graphite to metal; an alloy containing 15 percent molybdenum was more ductile than the alloy mentioned above. The 60Au-10Ni-30Ta and 35Au-35Ni-30Mo alloys were used to fabricate leak test specimens that consisted of a graphite tube with a brazed molybdenum cap at each end (ref. 154).

Recent research at ORNL has been concerned with joining graphite to INOR-8 (Hastelloy N), a nickel-base alloy with the composition 71Ni-17Mo-7Cr-5Fe (refs. 155, 156). The large difference between the expansion coefficients of graphite and INOR-8 results in cracking of the brazed graphite-to-INOR-8 joints upon cooling from the brazing temperature. Insert materials,

placed between the faying surfaces of the graphite and INOR-8 parts, minimize this problem; the expansion coefficient of the insert material should be between that of graphite and INOR-8. To investigate the suitability of refractory metals for this application, joints between the following metal combinations were brazed with a nickel-base alloy and the gold-nickel eutectic: INOR-8 to tungsten, INOR-8 to molybdenum, molybdenum to niobium, and tungsten to niobium. It was found that crack-free joints could be made with a ductile filler metal such as Au-18Ni, but not with the brittle nickel-base alloy. Joints between graphite and the refractory metals were also brazed with 70Au-20Ni-10Mo (very ductile) and 35Au-35Ni-30Mo (slightly ductile); with these joints, the ductility of the filler metal had little influence on cracking. Crack-free joints were produced between graphite and molybdenum and graphite and tungsten; the expansion coefficients of these metals are similar to that of graphite. Cracking was observed when graphite was brazed to niobium or tantalum, which have significantly larger expansion coefficients than graphite. On the basis of these studies, further work to join graphite to INOR-8 using molybdenum or tungsten as an intermediate material is currently underway.

In another investigation directed toward nuclear reactor applications, graphite was brazed to a structural alloy, Nilo-K; leaktight specimens were prepared to determine the permeability of graphite at high temperatures (900° C or 1652° F) and high pressures (ref. 157). Satisfactory tube-to-end cap joints were brazed with a titanium-cored silver-copper eutectic alloy. The graphite and Nilo-K workpieces were assembled and brazed in an evacuated silver envelope.

Several investigations to develop procedures to braze graphite to other materials have been associated with aerospace applications. In 1962, Ikeuye and Grow reported on developing filler metals to braze pyrolytic graphite to beryllium oxide (ref. 141). The three titanium-base alloys—93Ti-7Ni, 93Ti-7Cr, and 53Ti-47Cr—developed and evaluated during this program wet the graphite and beryllium oxide base materials in a vacuum or inert-gas atmosphere.

Difficulties were experienced because of the differing expansion coefficients of pyrolytic graphite and beryllium oxide; special joint designs were prepared to minimize the stresses established during the brazing cycle (fig. 20).

Two types of graphite have been brazed to the niobium-base alloy Nb-1Zr or Type 316 stainless steel for a space radiator (refs. 158 and 159). The graphite-metal combinations, the compositions of the brazing alloys, and the brazing temperature are shown in table 29; brazing proceeded in a vacuum of 10^{-5} torr. The brazing alloys, developed by the Oak Ridge National Laboratory, were deposited on the metal sub-

strates by plasma-arc spraying procedures; about 50 percent of the titanium in the 66Ag-26Cu-8Ti alloy and 25 percent of the beryllium in the 48Zr-48Ti-4Be alloy were lost during spraying; the alloy compositions were adjusted to compensate for these losses. The thermal stability and joint integrity were evaluated by aging and thermal cycling tests conducted in a vacuum of 10^{-5} torr; the test results are summarized in table 30. In additional aging tests, conducted to determine the long-time stability of the brazed joints, graphite-to-Type 316 stainless steel joints, brazed with 66Ag-26Cu-8Ti, were encapsulated, evacuated to 10^{-3} torr or below, and aged at 1350° F (732° C) for 250, 1000, and 4000 hours. Graphite-to-alloy Nb-1Zr joints, brazed with 48Zr-48Ti-4Be, were aged under the same conditions at 1500° F (815° C) for similar periods. The results of the aging tests indicated that the Ag-Cu-Ti alloy was not compatible with Type 316 stainless steel at 1350° F (732° C) for periods longer than 1000 hours; no difficulties were experienced with the graphite-to-alloy Nb-1Zr joint after the 4000-hour aging period.

Tungsten-to-graphite joints for service at temperatures up to 5000° F (2760° C) have been studied at Narmco Research and Develop-

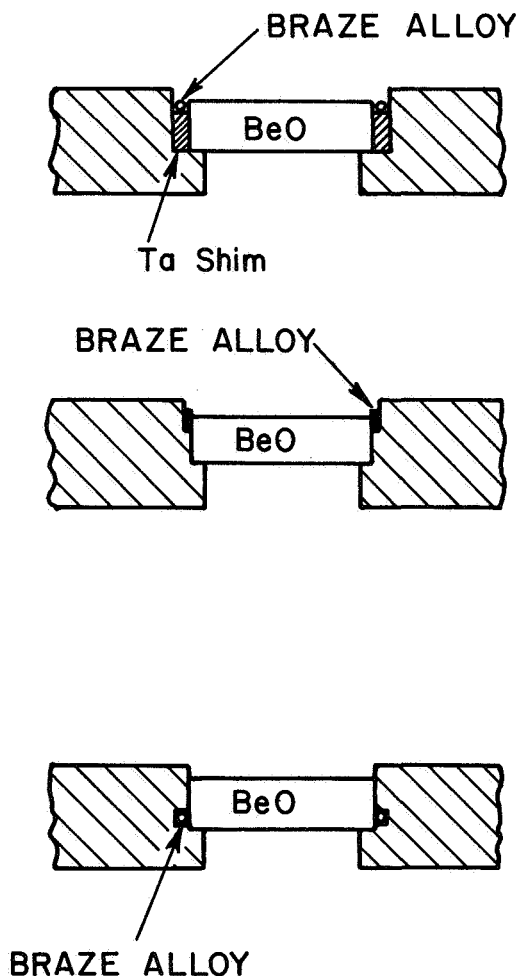


FIGURE 20.—“Frame” specimens modified to partially absorb BeO expansion as strain in the pyrolytic graphite (ref. 140)

TABLE 29.—*Graphite-to-Metal Joint Combinations*

[From ref. 159]

Material combinations	Brazing alloy, weight percent	Brazing temperature, °F
Graphite G to Cb-1Zr alloy.	66Ag-26Cu-8Ti.	1750.
	48Zr-48Ti-4Be.	1925.
	85Au-10Ni-5Fe.	2025.
Graphite G to Type 316 stainless steel.	Same as above.	Same as above.
Expanded pyrolytic graphite to Cb-1Zr alloy.	Same as above.	Same as above.
Expanded pyrolytic graphite to stainless steel Type 316.	Same as above.	Same as above.

TABLE 30.—*Thermal Stability Test Results of Graphite-to-Metal Joints*

[From ref. 159]

Material combination	Braze alloy	Metallographic analyses	
		After aging for 500 hours at 1350° F	After 500 thermal cycles at 350° to 1350° F
316 S.S.-graphitite G.....	66Ag-26Cu-8Ti	Crack near braze....	No cracking.
316 S.S.-expanded pyro- graphite.	66Ag-26Cu-8Ti	No cracking.....	No cracking.
Nb-1Zr-graphitite G.....	66Ag-26Cu-8Ti	No cracking.....	No cracking.
Nb-1Zr-expanded pyro- graphite.	66Ag-26Cu-8Ti	No cracking.....	No cracking.
316 S.S.-graphitite G.....	48Zr-48Ti-4Be	Crack near braze....	Crack near braze.
316 S.S.-expanded pyro- graphite.	48Zr-48Ti-4Be	No cracking.....	No cracking.
Nb-1Zr-graphitite G.....	48Zr-48Ti-4Be	No cracking.....	No cracking.
Nb-1Zr-expanded pyro- graphite.	48Zr-48Ti-4Be	No cracking.....	No cracking.
316 S.S.-graphitite G.....	85Au-10Ni-5Fe	Crack near braze....	Crack near braze.
316 S.S.-expanded pyro- graphite.	85Au-10Ni-5Fe	No cracking.....	No cracking.
Nb-1Zr-graphitite G.....	85Au-10Ni-5Fe	No cracking.....	No cracking.

ment (refs. 144 and 160). Much of the research was directed toward developing a suitable coating for the graphite and/or tungsten surfaces to enhance joining. The most successful coating, 60TaC-30WC-10ZrC, resulted from a mixture of tungsten and tantalum powders plus zirconium-hydride powder. The graphite surface was machined to a flatness of 200 microinch or less, coated with a wash coat of rhenium powder, painted with a slurry of tantalum, tungsten, and ZrH_2 powders, and dried in an oven at 150° F (65° C). The specimen was then fired at 5400° to 5500° F (2982° to 3038° C) in an argon atmosphere. The brazing alloy, 21W-79V, in the form of a mixture of the individual metal powders suspended in a suitable vehicle, was slurry-coated on the tungsten surface. After the coating was dry, the carbide-coated graphite and the filler-metal-coated tungsten parts were assembled and brazed in an argon atmosphere at 4200° to 4400° F (2315° to 2427° C); the parts were weighted to ensure contact during brazing. Some brazed specimens were also made with a 25W-75Re filler metal in the same manner as discussed

above. Thermal shock tests, the severest of which consisted of heating the specimen to a minimum temperature of 4425° F (2440° C) in slightly more than 10 seconds, followed by cooling to below red heat in 15 seconds, were conducted in the heat flux generated by a plasma-arc torch; no joint failures resulted. Joint tensile strengths of 530 psi at room temperature and 193 psi at 4000° F (2204° C) were obtained. In using the techniques discussed above to braze a simulated rocket nozzle configuration, some difficulty was experienced in maintaining good contact between the graphite backup structure and the tungsten liner; this problem was overcome by segmenting the graphite part.

Graphite was brazed to tungsten using pure titanium as the filler metal during an earlier investigation (ref. 161). Since titanium flowed sluggishly on tungsten and reacted quickly with graphite, it was necessary to preplace the filler metal in the joint and provide a reservoir of filler metal. The joints were brazed in an argon atmosphere at 3240° F (1782° C) minimum; the brazing time was minimized to retain maximum joint ductility.

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